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TECHNICAL PROGRESS REVIEW

REACTOR FUEL PROCESSING

Prepared by ARGONNE NATIONAL LABORATORY for the U. S. ATOMIC ENERGY COMMISSION

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APRIL 1958 VOLUME 1 NUMBER 2

TECHNICAL PROGRESS REVIEWS

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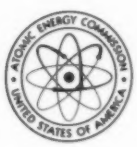
REACTOR FUEL PROCESSING

a review of recent developments prepared by

ARGONNE NATIONAL LABORATORY

APRIL 1958 VOLUME 1 NUMBER 2



foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the Division of Information Services of the United States Atomic Energy Commission. It is the second issue of this series which is intended to assist those interested in keeping abreast of important developments in this field. In each issue it is planned to cover those particular subjects in which significant new results have been obtained. The review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results where given represents the opinions of the editors of the review, who are personnel of the Chemical Engineering Division of Argonne National Laboratory. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

R. W. Cook, Deputy General Manager of the Atomic Energy Commission, speaking at the Atomic Industrial Forum in October 1957, discussed the present relation of industry and the AEC in the field of fuel reprocessing. The following is a summary of his remarks.[1]

In January 1956, the AEC announced a program to encourage private industry to build and operate chemical processing plants. At that time the Commission planned to offer certain AEC irradiated fuels as a guaranteed base load for a private plant as a concrete item of assistance to industry.

On Feb. 18 and Mar. 12, 1957, the Commission announced that it would enter into contracts with private reactor operators to provide for processing of their irradiated fuels on the basis of firm charges until such time as commercial facilities having the required processing capability became available.

Since the initial announcement in January, the Commission has been studying the terms and conditions under which the AEC could accept proposals for processing services on the base load for a commercial plant. In April 1957, a number of companies interested in this field were requested to submit comments on a proposed invitation containing the terms and conditions under which the AEC would accept proposals for processing the base load.

The proposed invitation for competitive proposals was generally unacceptable to industry for a number of reasons, and no alternative bases acceptable to the AEC were included in the replies received. It was the consensus of the companies that the income from the plant, using the AEC definition of reasonable cost, would be insufficient to provide an acceptable return on the capital investment required. The unknown increase in development costs when fuels are changed to more competitive ones, the complexities of the storage and disposal problem, and the probable rapid obsolescence of some of the processes selected for the plant were some of the specific deterrences noted by industry. The AEC does not wish to invite proposals from industry when there appears to be no reasonable chance that acceptable arrangements will result. Accordingly, the AEC does not intend to issue a formal invitation for proposals at this time.

This leaves the Commission with a problem of how to prepare for the processing of fuels returned from licensed reactors while still planning to have industry assume responsibility for processing private fuels at a later date. After a study of the possible alternatives, the AEC decided to process these fuels in existing developmental and production facilities for an interim period until industry builds plants for the recovery of source and special nuclear materials from licensed spent fuels.

Present plans do not contemplate processing these fuels in existing facilities beyond the expiration date of contracts with licensed reactor operators (June 30, 1967). Since it is the intention of the Commission not to stay in this business, every effort will be made to minimize such modifications as will be necessary to existing facilities and to postpone actual expenditures of funds until the latest possible date consistent with the need to keep recovery on a reasonably current basis. The Commission does not consider the use of existing AEC plants for performing recovery services desirable over the long term. This plan has been selected with the confidence that the economics of chemical processing will change and that the industry will build and operate processing plants in the near future. While the Commission does not plan to issue an invitation in the near future offering specific AEC assistance in the form of a base load, the way is open

at any time for industry to build and operate a processing facility subject only to the Commission's licensing requirement.

The Commission will continue to direct research and development effort toward both the immediate problem of modification of existing facilities and the long-range one of developing new low-cost processing methods. Work will also continue toward developing solutions to the waste storage and disposal problems.

In its January 1956 announcement the AEC noted that Commission facilities may be utilized by private firms for research and development and for training in connection with chemical processing. The full cost of such utilization would be defrayed by the user. This point is emphasized again since no one to date has taken advantage of the offer. The work experience program, or training program, offers the fastest and least expensive way to train personnel and obtain up-to-date technology in this field.

* * *

In the *U. S. Federal Register* of Dec. 28, 1957, the AEC published a schedule of guaranteed prices for U^{233}. The prices[2] quoted are those previously referred to on Mar. 3, 1956, but classified "Confidential — Restricted Data." The prices quoted are for uranyl (233) nitrate solution of concentration about 400 g/liter delivered to the USAEC between Feb. 1, 1957, and June 30, 1963. A number of product specifications are given.

The price established is $15 per gram of U^{233} and U^{235}, provided, however, that, when the combined content of U^{233} and U^{235} is less than 95 wt. % of the total uranium, the price of $15 per gram shall be reduced by the ratio of the per-gram price of U^{235} at the enrichment represented by the combined content to the per-gram price of U^{235} at 95 per cent enrichment of $17.11 per gram. An illustrative table of prices is included in the *U. S. Federal Register* and is reproduced here in Table I-1. Also in Table I-1 are given the published prices of U^{235} at these same enrichments. There does not appear to be any restriction on the U^{233} to U^{235} ratio.

The U^{235} price is for uranium hexafluoride; the U^{233} price is for an aqueous solution of uranyl nitrate. The radioactive specification on the U^{233} is such that the radiation at 1 ft from a quart bottle would be about 400 mr/hr (<1 hr working time per week).

In Vol. 1, No. 1, of this Review, mention was made of an article by Ullmann and Arnold[3] on the decay and storage requirements of highly irradiated fuel. Most of their attention was directed to transuranic elements. Their reasoning has been extended to the fission element, iodine,* by Levenson.[4] The following assumptions are made.

Table I-1 GUARANTEED FAIR PRICES OF U^{233} AND U^{235}

$U^{233} + U^{235}$ in total uranium, wt. %	Price, $/g		
	$U^{233} + U^{235}$*	Total* uranium	U^{235}†
100	15.00	15.00	
95	15.00	14.25	17.11*
90	14.96	13.46	17.07
80	14.90	11.92	17.00
70	14.84	10.39	16.93
60	14.77	8.86	16.85
50	14.69	7.35	16.76
40	14.58	5.83	16.64
30	14.41	4.32	16.44
20	14.12	2.82	16.12
10	13.40	1.34	15.29
5	12.24	0.61	13.96
1	6.64	0.07	7.58
0.7	4.93‡	0.035‡	5.62

**U. S. Federal Register*, Dec. 28, 1957.
†AEC Press Release, Nov. 18, 1956, statement by the President.
‡Calculated.

1. Uranium processed, 1 ton/day (minimum sized plant with chance of being economic)
2. Irradiation, 5000 Mwd/ton
3. Irradiation time, one year (average)
4. Retention of iodine in plant, 99.5 per cent
5. Allowable iodine discharge, 0.1 to 0.5 curies/day (in a semiremote location). Then

$$5000 \text{ Mwd/ton and } 1 \text{ ton/day} \cong 5000 \text{ g } U^{235}$$

consumed per day. I^{131} at 15 days after discharge for one year irradiation equals 0.027 atoms per 100 atoms fissioned.[5] Therefore

$$\frac{5000}{235} \times 6 \times 10^{23} \times \frac{0.027}{100} = 3.45 \times 10^{21} \text{ atoms}$$

$$\lambda_{I^{131}} \cong 1 \times 10^{-6} \text{ sec}^{-1}$$

*This fission product has always been troublesome from a disposal standpoint. The recent Windscale incident points up the problem.

$$\text{Curies at 15 days} = \frac{3.45 \times 10^{21} \times 10^{-6}}{3.7 \times 10^{10}} = 93{,}000$$

Curies discharged = $93{,}000 \times 0.005 = 450$

Decay factor required:

$$\frac{450}{0.5} = 900 \cong 10 \text{ half-lives}$$

$$\frac{450}{0.1} = 4500 \cong 12 \text{ half-lives}$$

Use 11 half-lives, 88 days; original cooling, 15 days; total, 103 days.

It may, therefore, be reasonably concluded that, with present processes and technology, iodine emission alone will dictate about 100 days cooling.

References

1. *Chemical Engineering Progress*, 53(12): 90 (December 1957).
2. *U. S. Federal Register*, Vol. 21, p. 1421, 1956. (Available from the U. S. Atomic Energy Commission, Division of Civilian Application, Washington 25, D. C.)
3. J. W. Ullmann and E. D. Arnold, Choosing Storage Time To Minimize Processing Costs, *Nucleonics*, 15(6): 80 (1957).
4. M. Levenson, Argonne National Laboratory, private communication.
5. L. Burris and I. G. Dillon, Estimation of Fission Product Spectra in Discharged Fuel from Fast Reactors, ANL-5742, July 1957. (Unclassified AEC report.)

The large number of proposed reactor designs and resulting variety of fuel types require a variety of processes for dissolution and pretreatment prior to processing.

Several new methods of fuel-element dissolution have been proposed.

Dissolution

Batch dissolution experiments[1] determined the optimum dissolution rate of aluminum-uranium fuel elements in nitric acid, with mercury and fluoride catalysts, to an acid-deficient solution. Under optimum conditions the average rate to a 4.0*M* aluminum–3.5*M* acid-deficient solution was 70 mg/(sq cm)(hr), and to a 3.0*M* aluminum–2.1*M* acid-deficient solution it was 196 mg/(sq cm)(hr). These rates are considered feasible for plant processes.

Further information was obtained on the feasibility of dissolution of Zircaloy clads in ammonium fluoride (Zirflex process).[2] Information was obtained on the fate of plutonium in this process. Plutonium(IV) nitrate was spiked into 6*M* ammonium fluoride to a concentration of 0.08 g/liter of plutonium. The results of boiling this solution 2.5 hr in contact with metallic uranium show that, at least for Pu(IV), losses of plutonium to the ammonium fluoride decladding solution will be minor but that conversion of fluorides of Pu(IV) to fluoride-free nitric acid soluble forms will be more difficult than that for U(IV).

Work has been performed[3] on dissolution of Zircaloy-2 in 77 per cent sulfuric acid–0.25*M* hydrofluoric acid. Average over-all dissolution rates of 600 mg/(sq cm)(hr) (90 per cent dissolved) were obtained holding the dissolving temperature below 150°C.

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1. R. L. Andelin, F. H. Tingey, and C. M. Slansky, Status Report on Studies of Uranium-Aluminum Alloy Dissolution to a Diban Dissolver Product, IDO-14407, June 17, 1957. (Unclassified AEC report.)
2. L. P. Bupp, Hanford Atomic Products Operation, Nov. 8, 1957. (Unpublished.)
3. L. P. Hatch et al., Brookhaven National Laboratory. (Unpublished.)

In this section an attempt is made to cover new work on existing separations processes and on proposed processes. The general areas covered are solvent extraction, precipitation, ion exchange, volatility and pyrometallurgical processing, corrosion, processing for homogeneous reactor systems, and instrument and equipment development. It is not expected that each subject will necessarily appear in each review.

Solvent Extraction

The major solvent-extraction processes, Redox and Purex, and modified processes to handle enriched fuels, have been in use at production plants for several years. These are highly successful processes and have been fully described in the open literature. The fact that the current literature may not contain many references to these processes should not be allowed to obscure the fact that these processes make up the bulk of the solvent-extraction operations within the nuclear energy program.

Process Modifications for Neptunium Recovery

Proposed modifications to the Purex and Redox processes to permit recovery of Np^{237} are being considered and tested. An information meeting[1] on neptunium recovery was held in March 1957 to discuss the future potential of neptunium recovery and modifications to the present processes which would enable recovery of neptunium.

In the Purex process it has been proposed that the flow sheet be adjusted so that Np^{237} would be extracted in the 1A extraction column and follow the uranium into the second uranium cycle, where, by the addition of a partitioning column, it would be selectively stripped from the uranium. By this procedure approximately 37 tons of uranium, 22 g Np^{237}, and 3.7 kg of plutonium were recovered in the Oak Ridge National Laboratory (ORNL) metal recovery plant from material that included ORNL tank farm waste, Chalk River uranyl nitrate, plutonium nitrate solutions, and miscellaneous other materials.[2,3] Uranium and neptunium product recoveries were 99.8 and 88 per cent, respectively.

Trialkylamines are under investigation for extraction of neptunium from nitric acid solution. These reagents appear to be uniquely suited for isolation of neptunium from Purex waste streams or for recovery of plutonium from the Plutonium Recycle Program (PRP) type fuel elements, where the uranium is considered to have no value, or as a replacement solvent for tributyl phosphate (TBP) in the Recuplex process.[4] The solvent is stated to provide good decontamination from fission products and to be highly resistant to radiation.[5]

Thorex Process

During the past several years, the proposed Thorex process has been a one-cycle process in which thorium (initially as metal or oxide) and U^{233} have been separated from each other and from fission products. A two-cycle co-decontamination flow sheet has been developed (see Fig. 1), which offers better fission-product decontamination and process flexibility, particularly in the processing of short-decayed material.[3,6] The Thorex pilot plant at ORNL was converted to accommodate this flow sheet, and five runs were made in which 5.5 metric tons of irradiated thorium was processed, with separation of 11.8 kg of U^{233}. Average gross gamma decontamination factors were 4×10^4 for thorium and 2×10^5 for uranium, both products meeting tentative activity specifications. Solvent-extraction losses averaged about 1.3 per cent for the thorium and 0.3 per cent for the uranium. A method for continuous interfacial solids removal was installed in the pilot plant and was satisfactory in a 2-in.-diameter pulse column test. This method consists in pumping a stream from the interface through a glass-fiber filter and a Selas separator and reintroducing the two streams into their respective phases in the column. Some difficulty has been experienced in activity build-up in the solvent.

Studies of Solvent Radiation Damage

An important factor in reprocessing nuclear reactor fuels by solvent extraction is the radiation damage to the process reagents (principally the organic solvents), especially in the case of short-cooled fuels, where the fission-product radiation is very intense. Two studies of the radiolysis of TBP systems were reported in the last period.

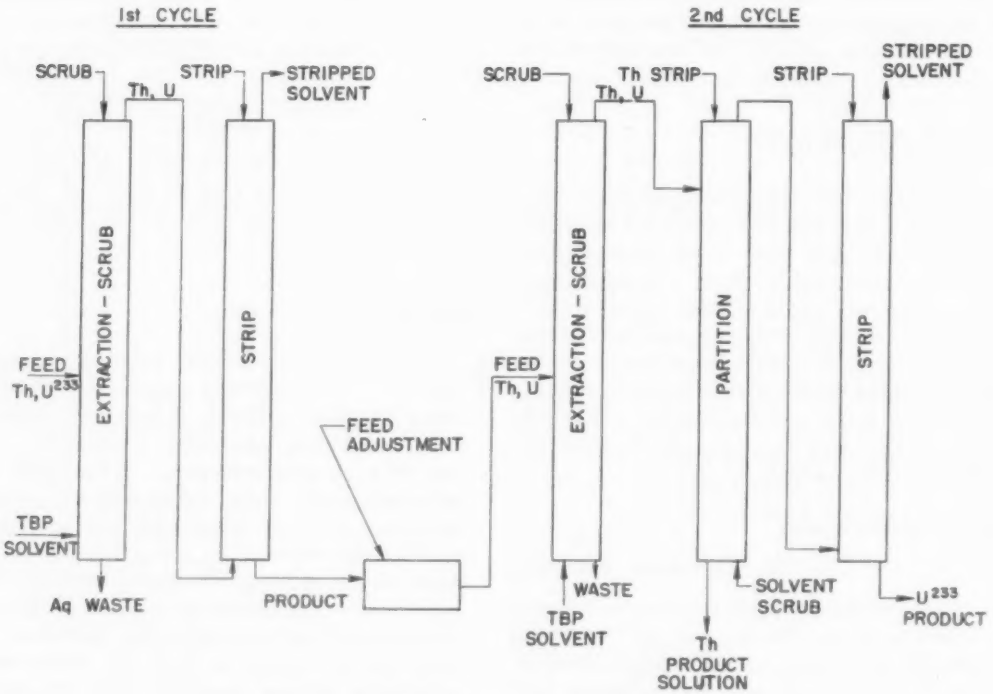

Fig. 1 — Thorex co-decontamination flow sheet.

The radiolysis of pure TBP and of mixtures of TBP with various diluents was studied by Burger and McClanahan[7] using Co^{60} gamma radiation. The liquid products from gamma radiolysis of TBP included dibutyl phosphate (DBP), butyl alcohol, monobutyl phosphate (MBP), butyl ether, phosphoric acid, hydrocarbons, and polymers. Dibutyl phosphate was produced in the largest yield, to the extent of 0.14 g/watt-hr of gamma energy absorbed by pure TBP. This corresponds to a G value (molecules of TBP changed per 100 electron volts absorbed) of 1.8. Saturation with water reduced the yield of DBP about 30 per cent. Dilution with a paraffin hydrocarbon did not change the radiolysis yield of DBP. Dilution with an aromatic hydrocarbon (benzene) reduced the yields, whereas dilution with carbon tetrachloride greatly increased the TBP decomposition. In the latter case a postradiation effect was observed.

The chloride yield from TBP–carbon tetrachloride mixtures was constant at about 0.07 g/watt-hr absorbed by the carbon tetrachloride for mixtures containing from 25 to 100 per cent carbon tetrachloride. Phosgene and hexachloroethane were also produced. The presence of uranium and nitric acid in the TBP systems reduced the yields of both DBP and chloride ion.

The radiation decomposition of TBP solutions of interest in solvent-extraction processes was studied by Williams and Wilkinson[8] using fast electrons from a Van de Graaff machine. In all cases radiation damage to the solvent led to the production of gas and acid phosphate, and the yields were measured for both TBP and TBP–odorless kerosene solutions.

Irradiation of TBP and TBP-kerosene mixtures gave a volatile gas consisting mainly of

hydrogen with small amounts of methane and C_2 hydrocarbons. Unsaturated hydrocarbons consisting of more than two carbon atoms were also identified. The presence of dissolved nitric acid, water, and uranyl nitrate resulted in a decrease of hydrogen production, with the formation of nitrogen oxides and carbon dioxide.

The acid phosphate produced was found to be a mixture of DBP and MBP. Both these acids were formed simultaneously with a yield ratio of 9 to 1 in favor of DBP. Acid phosphate production in TBP increased if nitric acid was present in the solvent, but addition of uranyl nitrate brought about a decrease in yield. TBP containing water in a 1 to 1 molar ratio gave an acid phosphate yield of approximately one-half the value for the dry solvent.

The irradiation of dilute solutions of TBP in nitric acid gave low rates of decomposition, particularly if the concentration of nitric acid was below 8*N*. An appraisal has been included of the chemical effects of radiation in a plant based on the use of 20 per cent TBP–kerosene as a solvent for processing enriched fuel elements.

At ORNL an attempt is being made to correlate investigations[9] on solvent radiation damage which have been carried out at the various atomic energy sites. Investigations of solvent radiation damage which are under way include (1) further investigation of the degradation products of diluents, (2) a comprehensive survey of alternate diluents for TBP, (3) investigation of protective agents that will decrease the degradation of solvent for a given amount of radiation, and (4) the fundamental process of TBP degradation by radiation.

Processing New Fuels

Chemical flow sheets have been developed for solvent-extraction processing of the Army Package Power Reactor (APPR) fuel and Atomic Power Development Associates (APDA) core and blanket material.[3] The APPR fuel[3] is a stainless-steel–clad stainless-steel–U^{235} alloy, whereas the APDA fuel[3] is a Zircaloy-2–clad uranium–10 wt. % molybdenum alloy. The APDA blanket is stainless-steel–clad uranium. All use TBP as the extractant.

Testing of New Solvents

Testing of various organic nitrogen compounds (alkyl amines) and organic phosphoric acids is continuing at various sites for application to purification and recovery of nuclear metals. One such application is in ore processing. Such extraction agents are also being investigated for their utility in the extraction of rare earths, zirconium, hafnium, and nickel from aqueous solutions.

Higgins, Baldwin, and Ruth[10] at ORNL and Burger[11] at Hanford Atomic Products Operation (HAPO) demonstrated that the dialkyl alkyl phosphonates are generally more powerful extractants than the alkyl phosphates. Equilibrium data are presented by Siddall[12] for the distribution of uranium and other actinide elements, zirconium, and nitric acid between aqueous solutions and dibutyl phosphonates diluted with dodecane.

1. *Application of New Solvents to Ore Processing.* Further work was reported[3] on the Dapex process, originally designed for the selective recovery of uranium from ore acid leach liquors by extractions with kerosene solutions of appropriate organic phosphoric acids. It can be modified for the recovery of vanadium and possibly thorium. Commercial plants using the Dapex process for uranium recovery have been operating since September 1956; they are the Climax Uranium Company, Grand Junction, Colo., and the Kerr-McGee Oil Industries, Ship Rock, N. Mex. Other commercial plants are being constructed at Rifle, Colo., and at Gunnison, Colo. Investigations of this process, both on a laboratory scale using bench mixer-settler equipment and on an engineering scale, are being pursued at ORNL.

An evaluation of various amines and organic phosphates as uranium extractants from sulfate leach liquors is also reported.[13–15] Pilot plant results on the use of an amine solvent-extraction process for ore recovery[16] and on the use of an alkyl phosphate[17] are reported.

A process for the recovery of uranium from ores by direct leaching with organic solutions containing alkyl phosphoric acid and sulfuric acid is also reported.[18] The process is applicable to carnotite ores.

In the course of their systematic study of organic complexing agents for uranium, Blake and co-workers[19] found the trialkylphosphine oxides to have a very high extraction coefficient for uranium. This reagent has also been found to extract chromium in the hexavalent state,

providing an analytical means of separating Cr^{+6} from Cr^{+3}, which is unextractable.[20]

Fundamental Solvent-extraction Studies

Equilibrium distribution data for Purex and similar extraction processes have been published.[21] Distribution of uranium, nitric acid, and thorium are reported between nitric acid and TBP-ultrasene (a high boiling kerosene) systems.

A series of papers dealing with the extraction of various metals in nitrate systems by TBP has recently been published in the *Journal of Inorganic and Nuclear Chemistry*. These were issued under the general title "Tri-n-Butyl Phosphate as an Extracting Agent for Inorganic Nitrates."[22-26]

The partition of tracer-level lanthanides, yttrium, and americium between various TBP phases and aqueous nitric acid phases has also been studied radiometrically as a function of solvent concentration, nitric acid concentration, by Peppard and co-workers.[26]

In addition to TBP, various mono- and dialkyl phosphates are being investigated for, or used in, the various nuclear metal recovery and purification operations (see p. 7). For example, the use of dodecyl phosphoric acid for recovery of uranium from sulfate leach liquors was reported in Vol. 1, No. 1, of this Review.[27] Peppard and co-workers[28] have recently published work on the use of dialkyl phosphates for extraction of the lanthanide elements and for isolation of berkelium.[29]

Plant and Equipment Design and Operation

1. *Nuclear Safety — Criticality.* The change to a co-decontamination flow sheet by ORNL Thorex Pilot Plant resulted in plant changes which increased the size of some process vessels and changes in chemistry which increased maximum possible U^{233} concentrations in some process streams. The U^{233} concentration in feed solutions will also be increased when longer-irradiated thorium slugs are processed. Because of these changes a criticality study[30] was made.

The results[30] are based on calculations in which the product of the resonance calculations and the fast fission effect was assumed to be unity. A comparison of calculated results with experimental data indicates the calculated results to be conservative in the range of concentrations studied. A U^{233} concentration of 10,000 g/ton of thorium (10,000 g/ton) was used as a basis for evaluation. This is a factor of 2 greater than actual levels expected.

Critical safety was designed into the equipment of the uranium isolation system, the third uranium cycle, and uranium storage facility by limiting the size and capacity of the equipment. There are, however, connections between these systems and the large process equipment which present potential hazards. To reduce these hazards, a lockout system was provided on the exit streams from all geometrically safe equipment to impede the transfer of concentrated uranium solutions to nongeometrically safe equipment.

The maximum concentrations of U^{233} in Thorex process equipment should be limited as follows to ensure safety from a criticality incident.

1. Large process tanks (18 to 20 in. diameter), 10 g/liter
2. Thorium process evaporators (because of size of tanks to which concentrated solution is transferred), 10 g/liter
3. Pulse columns (fixed by diameter of disengaging sections), 15 g/liter
4. First-cycle "A" column accumulator (18 in. diameter by 33 in. high), 15 g/liter
5. First-cycle "A" column product stand pipe (2 in. diameter), critically safe at any uranium concentration

The first-cycle "A" column organic phase product (1AP) stream overflows to a surge tank consisting of a 15-ft section of 2-in.-diameter pipe with an enlarged section 22 in. in diameter and 48 in. high which limits the concentration to 10 g/liter. The second-cycle "B" column organic phase product (2BU) stand pipe is a section of 2-in.-diameter pipe with an enlarged section 10 in. in diameter and 10 ft long. The maximum safe uranium concentration in the enlarged section is 25 g/liter.

The uranium isolation system and third uranium cycle were designed to be critically safe with uranium concentrations up to 350 g/liter by limiting the size and capacity of the equipment.

A number of special operating procedures are used to ensure safety from criticality incidences. These include:

1. The steam supply to jackets on all large process vessels that could contain uranium at a uranium to thorium ratio greater than 5000 g/ton should be disconnected. Steam recircula-

tion jets have been disconnected from all tanks except two which require heating for normal operation. By use of the recirculation jets the contents of these tanks can be heated but not concentrated.

2. If it is necessary to add uranium solution more concentrated than 10 g/liter to a large process vessel, sufficient initial volume should be provided in the tank to give a final concentration less than 10 g/liter. Also, no more than 300 g of uranium should be added at one time, with a period of agitation between additions.

3. Material balances are kept around make-up tanks and evaporators to prevent concentration from exceeding safe limits.

4. Effluent lines from sources of high uranium concentration solutions to tanks not of geometrically safe dimensions are locked out, and the key is kept by the supervisor.

Whenever a modification to a process or to process equipment occurs in a fuel processing plant, a review of criticality considerations is necessary. A variety of means are available to the designer and operator to reduce criticality hazards. Good operating practices are necessary because it is not always practical or possible to design a plant that is completely safe geometrically.

2. *Shielding.* The conclusions from a recently completed study[31] of radiation exposure, process activity levels, and costs in relation to the shielding in a separations plant at Savannah River Operations Office follow.

1. In a building as large and costly as 221F (Chemical Separations Plant) at Savannah River, the relative saving in costs by reducing the shielding by a $\frac{1}{10}$-value layer, or even a $\frac{1}{50}$-value layer, would be only a small percentage of the total building costs or annual operating costs; however, the absolute dollar savings would be considerable.

2. Radiation values at the outside of the shielding walls are materially changed with a relatively small change in shielding thickness.

3. There is no gradual reduction in radiation level within a process cycle, i.e., a section with a high radioactivity may be followed by a section with a much lower level of radioactivity which, in turn, may be followed by a section of high radioactivity. It was, therefore, concluded that, for economy of construction and flexibility of operation, the shielding wall for a canyon may as well be the same thickness for its full length. However, in later process cycles, after the more radioactive impurities have been removed, the material being processed is considerably reduced in radioactivity, and the later process cycles may well be conducted in a canyon with thinner shielding walls. In designating the thickness of a shielding wall, consideration should be given to the possibility of using supplementary shielding such as steel plates attached to the outside of the shielding wall for those few sections in either canyon with the highest radioactivity.

3. *Equipment Design—Rotary Disk Contactor.* A rotary disk contactor is a mechanically agitated gravity-flow column. A number of disks are mounted on a single rotating shaft. The column is divided into compartments by ring type baffles. It is claimed that this contactor can be scaled up to comparatively large diameters without undue loss of extraction efficiency. Recently an advertisement in *Chemical Engineering* mentioned the installation of a 22-ft-diameter unit at an oil refinery.

Flood-point and mass transfer data have been obtained on a 24-in.-long 3.0-in.-diameter column.[32] For most measurements the baffle inside diameter was 2.25 in. One set of data was obtained at 2.0 in. Disk diameters were varied from 1.0 to 2.0 in., and spacing was varied from 0.5 to 4.0 in. For flooding data, the systems studied were water-toluene, water–butyl acetate, water-isooctane, water-benzene, and water–white oil. Acetone was added as a third component for mass transfer studies.

4. *Flow Colorimeter for Measuring Uranium Concentrations in Process Streams.* A flow colorimeter has been developed to measure the uranium concentration of uranyl nitrate solutions.[33] A collimated light beam from an incandescent bulb passes through a sample cell. A combination of beam splitter and interference filters then divides the beam into two parts. One part is composed of frequencies absorbed by uranyl ion, and the other part is composed of frequencies transmitted. The uranyl ion concentration is determined by comparing the intensities of the two parts of the beam. Turbidity, window fouling or darkening, and changes in light intensity, which affect both parts of the beam equally, show up only as second-order effects.

The sample cell is easily decontaminated. Windows of radiation-resistant glass are used

and are readily cleaned or replaced. The optical path length is $\frac{3}{8}$ in.

Aqueous solutions with uranium concentrations between 45 and 55 g/liter were measured in the laboratory with a precision of ±1 per cent. Other comparable concentrations can be measured by changing the optical path length and the electronic gain.

The instrument operated satisfactorily for four months in the metal recovery plant at ORNL, where it was used to measure concentrations between 26 and 36 and 45 and 55 g/liter. During this plant service, the estimated precision was ±3 per cent.

In both plant and laboratory service the instrumental variation and drift over a 24-hr period were equivalent to a change of uranium concentration of less than ±1 g/liter.

Precipitation

Precipitation is the oldest of the separation procedures employed in fuel reprocessing. Although it has been largely supplanted by other processing techniques, precipitation is still employed in separation procedures not readily adaptable to solvent extraction or ion exchange. Since it is inherently a batch procedure, it is frequently used in processes whose scale is not sufficiently large to warrant continuous operation. It is also a useful adjunct to solvent extraction for the removal of elements not easily separated in the extraction process.

Separation of Ba^{140} from MTR Fuel

A new facility for the production of Ba^{140} has recently been placed in operation at the Idaho Chemical Processing Plant (ICPP) to supplant a facility operated at ORNL from 1945 to 1956. The process used is called "RaLa," an abbreviation for radioactive La^{140}, which is the decay product of Ba^{140}. A single spent Materials Testing Reactor (MTR) fuel assembly[34] constitutes the charge material for each run, in which 25,000-curie batches of Ba^{140} are produced.

The fuel assembly is dissolved in sodium hydroxide solution, leaving uranium and most of the fission products as insoluble precipitates. The insolubles are separated by centrifugation and dissolved in nitric acid. The Ba^{140}, together with added inactive barium carrier, are precipitated by evaporation and by the addition of fuming nitric acid. To separate strontium from the barium, the precipitates are dissolved in water and converted to chromates by the addition of sodium chromate. Barium chromate is selectively precipitated by pH adjustment. The barium precipitate is metathesized to the nitrate form and redissolved in fuming nitric acid. Final purification is effected by precipitation of barium nitrate by the addition of water. Barium nitrate is redissolved in water and transferred to a drying cup where water is evaporated, leaving dry barium nitrate product.

The start-up program in the new RaLa facility included operations with both active and inactive material to develop successful operating techniques. The start-up program demonstrated that the processing of short-cooled MTR fuel to produce 25,000-curie batches of Ba^{140} can be conducted adequately with no deleterious effects of radiation on the chemical flow sheet. A product of acceptable activity and purity was produced, with product recovery efficiencies of about 62 per cent.

The major items of process equipment in the RaLa facility are the dissolving vessel and the centrifuge. Most of the process operations are carried out in the centrifuge itself, which is a complex design to permit remote operation with low product losses. The centrifuge is essentially a standard bowl type machine adapted for remote operation through the 6-ft-thick concrete shielding walls. The bowl case is modified by closing the shaft aperture with a carbon seal to prevent the dissipation of air-suspended particulates and mist. The bowl case and bowl are equipped with jackets, to which water and steam may be supplied for temperature control during operation. A periscope can be inserted through an access hole for viewing the inner bowl wall to determine the status of bowl-cleaning operations. The bowl and case are provided with a number of spray heads for removing radioactive deposits preparatory to maintenance work. All wetted or exposed parts of the centrifuge are fabricated of stainless steel.

The slurry to be centrifuged is fed continuously to the bowl. The supernatants flow over the bowl weir, and the residual 5-liter heel is removed by skimming. The skimming is so complete that 30 ml or less of solution is left in the bowl. Each skimmer discharges into a vented reservoir called a "kidney," from which the liquid is drained to the proper vessel. The product cake is dislodged for washing or dissolving by a cutter nozzle that sprays a wash or

dissolving solution against the bowl wall in each of the sections formed by the bowl baffles. A drawoff line can be lowered into a depression in the bowl to remove the contents by suction.

The 5-hp d-c motor, which develops 1500 G's centrifugal force, is enclosed in a stainless-steel shroud to which air is circulated for cooling. Lubrication is by a once-through gravity oil system.

The centrifuge unit cost was approximately $30,000, excluding the cost of installation labor.

Zirconium-Niobium Scavenging

A major problem in nearly all solvent-extraction processes is the achievement of adequate separation[35] from ruthenium, zirconium, and niobium. The difficult chemical behavior of zirconium and niobium results from strong hydrolytic tendencies and ease of radiocolloid formation, with subsequent low solubility and erratic behavior in aqueous-organic phase separation during solvent extraction. As a result of these difficulties a head-end scavenging step is often used to remove the bulk of the zirconium and niobium prior to solvent extraction.

In laboratory studies it was found that 90 to 99 per cent of both zirconium and niobium could be removed from hot (100°C) dissolver solution by manganese dioxide formed in situ by the reduction of potassium permanganate. On a semiworks scale it was observed that appreciable amounts of other fission products ranging from 1 to 10 per cent for ruthenium to as much as 40 per cent for cerium were removed also. The manganese dioxide, when precipitated from solutions having acidities in the range of 0*M* to 0.2*M* nitric acid, was very finely divided, and in this form was a very efficient scavenger. Centrifugation was the preferred method for separating the precipitate.

Other agents, such as filter clays and diatomaceous earth, were also found to scavenge zirconium-niobium. However, potassium permanganate can be made to serve a double purpose since it is capable of oxidizing fission-product ruthenium to ruthenium tetroxide, which can then be removed from the feed solution by volatilization. Moreover, agents such as the filter clays are essentially insoluble in most aqueous mediums and must be removed from the centrifuge by physical rather than chemical means. Manganese dioxide, however, can be converted to the soluble manganous ion by common reducing agents such as chromic ion and removed as a solution.

Ion Exchange

Additional research work is being done on application of ion exchange in the atomic energy industry. Recent data have been presented for application of anion-exchange resins to fission-product decontamination of PRP fuels.

The feasibility of obtaining complete fission-product decontamination of PRP fuels by anion exchange was tested in a two-cycle run.[5] A feed solution containing 7.7*M* nitric acid, 104 g/liter uranium, 0.47 g/liter Pu(IV), 1.1×10^9 counts/min/ml zirconium-niobium gamma activity, and 1.6×10^7 counts/min/ml ruthenium-rhodium gamma activity was prepared from Purex dissolver solution. This feed solution was processed through two Dowex-1, X-4 (100 to 200 mesh) column cycles with a two-cycle gross gamma decontamination of 3×10^7. The new Dow anion-exchange resin, Dowex-21K, was also tested for efficiency of fission-product decontamination and found to be substantially poorer than Dowex-1, X-4 (e.g., zirconium-niobium decontamination was 950 for Dowex-21K as against 7500 for Dowex-1, X-4). Separation of uranium from plutonium by a factor of 10^6 was found in a series of seven runs using Dowex-1, X-4 (50 to 100 mesh) resin and an elevated temperature (60°C).

Dowex-1, X-4 (50 to 100 mesh) anion-exchange resin was found to be severely damaged upon standing in contact with static 7*M* nitric acid at elevated temperature. After a contact time of 14 days at 60°C, the resin had swollen and become so gelatinous that it was not usable. The solution in contact with this resin was found to contain large quantities of nitrite. In order to avoid this nitrite build-up, the static experiment was repeated with sulfamic acid added, and a column experiment was set up in which fresh nitric acid flowed through the resin at elevated temperature. The flowing system was adjusted so that the acid had a 10- to 15-min residence time in contact with the resin. Neither the resin in contact with the flowing 7*M* nitric acid nor the resin in contact with the static 7*M* nitric acid containing sulfamic acid shows any physical damage after 21 days at 60°C. No data are available on the effect of the presence of sulfamic acid in the feed solution on decontamination factors.

Fluoride Volatility Processes

A number of nonaqueous fluoride volatility processes have been proposed with the aim of yielding the desirable end product uranium hexafluoride more directly than is possible with aqueous processes. In these processes fluorination is used as a first step, and decontamination is subsequently effected by fractional distillation or absorption-desorption applied to uranium hexafluoride. Low-temperature liquid halogen fluoride dissolutions and high-temperature fused-fluoride-salt dissolutions have been studied at several sites.

Fused-salt Processes

The fused-fluoride process is considered promising for recovery of enriched uranium from zirconium-uranium alloy fuels. In this process the alloy is dissolved in a molten sodium fluoride–zirconium fluoride salt bath at about 600°C with a hydrogen fluoride sparge, and uranium hexafluoride is produced and volatilized with a fluorine sparge.

A pilot plant facility for recovery of irradiated uranium by the fused-fluoride volatility process has been installed at ORNL. The basic features of the fluorination and uranium recovery systems have been described,[36] and the equipment has been undergoing tests with unirradiated uranium.

In fluorinator tests salt batches containing 10 kg of uranium (as uranium tetrafluoride) were sparged with fluorine and nitrogen. The off-gas was put through a sodium fluoride absorber, and the product uranium hexafluoride was collected in cold traps. In the first eight runs, as high as 98.5 per cent of the uranium was collected as product, with as little as 0.006 per cent being unrecoverable losses.[37]

In a run with a fluorine sparge of 15 to 20 liters/min (STP), a total fluorine to uranium mole ratio of 3.2 to 1 reduced the uranium content of the salt to 88 ppm. Approximately 1 hr was required for this step. A subsequent 30-min sparge[38] with dry nitrogen reduced the uranium in the waste salt to 4.5 ppm.

Considerable carry-over of salt during runs was observed. Tests showed that volatilization of zirconium fluoride was of much greater significance than salt entrainment at the low flow rates (less than 1 scfm being used).[39]

The available salt contained 500 to 1000 ppm chromium fluoride (CrF_3), which was volatilized in the fluorine sparge. This material was deposited downstream and plugged a micrometallic nickel filter. In scouting experiments to find a suitable filter, sodium fluoride pellets appeared to remove both zirconium and chromium more efficiently than nickel mesh.

A charge of uranium hexafluoride was absorbed on sodium fluoride in an absorber unit and held there for three days at 300°C in a test of decomposition. Desorption in a nitrogen stream at 400°C recovered 70 per cent of the uranium. Then fluorine passed through for 1 hr at 400°C removed the remaining uranium, except for 0.9 per cent fixed on the bed. This method may be used to reduce fluorine consumption during desorption.

An L-nickel fluorinator (Mark-II) has been installed at Argonne National Laboratory (ANL) for use in pilot plant studies of the fused-fluoride volatility process. Also a graphite dissolver,[40] being prepared by Horizons, Inc., Cleveland, Ohio, will be installed in 1958 for use in studying this process.

Bromine Trifluoride Process

In one of the low-temperature fluoride volatility processes, bromine trifluoride is used for the direct fluorination of uranium metal. Product uranium hexafluoride is purified and decontaminated by fractional distillation. The plutonium fluoride and fission-product fluorides are concentrated as nonvolatile residues. Subsequent recovery of plutonium can be achieved by an aqueous wash with solvent-extraction decontamination or by nonaqueous fluorination to form volatile plutonium hexafluoride.

1. *Interhalogen Pilot Plant Studies.* Recent pilot plant dissolution studies on this process[41] were referred to previously. A report has been published[42] on the incident in this pilot plant which occurred May 15, 1957. A series of five explosions occurred, resulting in the rupture of the containment walls of one of the canned-rotor pumps and the release of process fluid. This was the only point of rupture in the system.

Examination of the monel dissolver showed dimensional changes, apparently due to high pressures, and fused interior portions due to high temperatures. The dissolver pressure relief system appeared to have functioned cor-

rectly. It consisted of a rupture disk followed by a self-closing type of pressure relief valve.

The cause of the explosion is not certain since uranium ignitions under these liquid-submerged conditions have not occurred previously. Early work at ANL[43] studied uranium ignition in bromine trifluoride, bromine pentafluoride, chlorine trifluoride, and fluorine. It is considered likely that a gas-phase reaction between uranium and interhalogens was brought about by the carrying of some uranium metal out of the liquid by a slug feeder device that was used periodically to follow the dissolution rate. Detailed data and recommendations for safe operation are given.[43] Laboratory studies pertinent to ignition and dissolution phenomena are planned at Brookhaven National Laboratory (BNL).

Process Chemistry of Fluoride Systems

1. *Dissolution of Zirconium in Fused Salt.* Further studies[44] were conducted on the dissolution rates of zirconium and zirconium alloys in molten sodium fluoride–zirconium fluoride at 600°C.

Earlier tests at modest sparge rates had indicated that the dissolution rate increased as the 0.25 to 0.3 power of the hydrogen fluoride sparge rate. The apparatus described earlier[45] was used in these experiments with the modification that only one coupon was used and the draft tube was removed. At increased sparge rates the dissolution leveled off at about 0.50 mm/hr.

A few tests were made to compare the dissolution rates of zirconium metal with several zirconium alloys. Under comparable conditions pure zirconium, Zircaloy, Zircaloy-2, Zircaloy-3, and a 4.2 per cent uranium–2.4 per cent tin–zirconium alloy showed similar dissolution rates, all in the range 0.26 to 0.31 mm/hr.

A series of standard dissolution runs were made using Zircaloy-2 to measure the effect of variations in the melt composition on the dissolution rate. The concentrations were limited to those sodium fluoride–zirconium fluoride solutions that remain liquid at 600°C. Results show a twofold increase in dissolution rate as sodium fluoride composition is increased from 45 to 63 mole %. ORNL data[46] show a 10-fold increase in dissolution rate in going from a 50 to 62 mole % sodium fluoride.

2. *Dissolution of Stainless Steel in Fused Salt.* An investigation was made of the dissolution of type 347 stainless steel by reaction with anhydrous hydrogen fluoride in the presence of a 53 mole % sodium fluoride–47 mole % zirconium fluoride mixture. The dissolution rate was slow, with preferential attack of the chromium, leading to disintegration rather than smooth dissolution. Metallic nickel was found in the melt after a 15-hr test dissolution[47] at 700°C. Solubility of nickel fluoride in the fused salt at 700°C was found to be only 0.10 wt. % in the presence of the other constituents of 18-8 stainless steel.[38] It is concluded that dissolution of 18-8 stainless-steel fuel elements under these conditions is impractical.

3. *Volatilization of Uranium Hexafluoride from Fused Salts Containing Potassium Fluoride.* An alternate method previously proposed for conversion of uranium or uranium alloys to uranium hexafluoride consists in converting the uranium to the tetrafluoride by reaction with fused potassium bifluoride, followed by a fluorination step to volatilize uranium hexafluoride. This liquid-phase reaction could be carried out at 300°C, where the dissolution pressure is low.

It had been shown previously[48] that uranium hexafluoride reacts with potassium bifluoride at 80°C, forming a stable, nonvolatile compound that probably has the composition KUF_7. Additional tests were performed which showed that this reaction compound was stable at least up to 600°C and that uranium hexafluoride was not readily volatilized[44] from potassium bifluoride melts at 300°C.

4. *Volatilization and Absorption of Fission Products from Fused Salt.* In the fused-salt process uranium hexafluoride is volatilized from the fused salt with a fluorine sparge. The manner and extent of fission-product volatilization are being studied. Most activity in the fluorination step occurred during the uranium hexafluoride volatilization. Micrometallic filtration of the process gas stream removed zirconium and niobium from the product but not much ruthenium. The transfer of zirconium activity corresponded to that expected from the vapor pressure of zirconium fluoride over fused salt. Fluorine sparging transferred more activity than nitrogen.[38]

Further confirmation was obtained that the chief activity transfer in the fluorination of fused salt occurs during uranium hexafluoride volatilization. This was true, not only for the fission products, whose fluorides are volatile, but also

for the rare earths, whose fluorides are relatively nonvolatile. The reason for this is not clear. Plutonium was the only contaminant whose fluoride volatilized significantly after uranium hexafluoride evolution ceased.[37]

Comparison of results of laboratory tests on desorption of uranium hexafluoride from the $UF_6 \cdot 3$ NaF complex with a theoretical analysis of the problem was made. Results indicate that desorption is possible under a variety of conditions, provided the total sweep gas volume is adequate, and that decomposition of U(VI) to U(V) is low, even with nitrogen sweep gas, if the time is short.

Encouraging results were obtained in using the solid absorbents alundum or calcium fluoride at 100°C and sodium fluoride at 400°C in removing fission products, plutonium, and chromium fluorides from the uranium hexafluoride gas stream.

Earlier data[49] showed fission-product niobium from an irradiated sample of zirconium-uranium alloy to be volatilized from a sodium fluoride–zirconium fluoride melt by hydrogen fluoride sparging at 600°C. This is consistent with the literature,[50] wherein niobium metal is reported to be converted to volatile niobium pentafluoride by hydrogen fluoride. Additional tests were made showing that macro amounts of niobium pentafluoride can be transferred quantitatively through nickel equipment as a gas. Also niobium pentafluoride was removed effectively from a stream of hydrogen fluoride carrier gas at 250 to 275°C by a bed of sodium fluoride.[44] Further tests are planned to determine the effect of fission-product concentration. This method is considered promising for cleanup of hydrogen fluoride recovered from the dissolution step of the fused-fluoride volatility process. A similar decontamination process for uranium hexafluoride has been demonstrated previously.[51]

5. *Plutonium Hexafluoride Studies.* The fluorination of plutonium to the hexafluoride and its subsequent separation from nonvolatile fission-product fluorides by volatilization represents a possible approach to the decontamination and recovery of plutonium from irradiated fuels. The reaction of dilute plutonium-uranium alloys with bromine trifluoride produces plutonium tetrafluoride together with uranium hexafluoride and bromine.[52] Therefore a study of the fluorination rates of plutonium tetrafluoride is of interest to a volatility separations process.

An experimental apparatus was built, and a procedure for fluorinations was established;[53] early rate data[52,53] indicated that plutonium tetrafluoride prepared by the high-temperature hydrofluorination of a plutonium compound reacted at a lower rate than that obtained as a residue from the bromine trifluoride alloy reaction, which was carried out at room temperature.

Further work confirmed the higher fluorination rates for the dissolution residues, which were found to be very finely divided. Rate data at 1 atm fluorine were satisfactorily correlated on a diminishing sphere model[54] and by an equation of the type

$$\log r = A - \frac{B}{T}$$

where r is the fluorination rate in milligrams per square centimeter per hour, the area term referring to exposed surface, and T is degrees Kelvin.[40] The values of the constants A and B and the activation energy derived from an Arrhenius plot are as follows:[40]

Type of PuF_4	A	B	$\Delta E \pm \sigma$, kcal/mole
Dissolution residue	5.986	2253	10.4 ± 0.6
High temp., type 1	5.857	2545	11.7 ± 0.1
High temp., type 2	5.918	2719	12.5 ± 0.4

Laboratory tests were made of the transfer of plutonium hexafluoride in the vapor phase.[55] Plutonium hexafluoride is decomposed by heat, by its alpha radiation, and by reactions with most materials of construction. Laboratory experiments showed that plutonium hexafluoride vapor could be transferred satisfactorily through well-fluorinated nickel equipment in a stream of fluorine or helium. The decomposition product of plutonium hexafluoride was refluorinated at 250°C by fluorine. Equipment and procedures are described.

Pyrometallurgical Processing

Pyrometallurgical processing methods are under investigation at several sites because of promise they offer in reducing processing costs through ability to process short-cooled mate-

rial. A description of the various pyrometallurgical operations being considered was presented in Vol. 1, No. 1, of this Review and will not be repeated here. Two pyrometallurgical pilot plants are now being designed, one at ANL for processing fuel from the EBR-II fast breeder reactor and the other at Atomics International Division of North American Aviation, Inc.

Melt Refining Process Studies

The melt refining process or, as it has previously been called, the oxide drossing process will be used for rapid purification and recovery of discharged EBR-II fuel.[40] It consists in melting the decanned fuel pins in an oxide crucible, probably zirconia, and holding at a temperature of 1300 to 1400°C for 3 to 5 hr. Volatile fission products (xenon, krypton, and cesium) are boiled off, and, by reaction with the crucible material, the very reactive fission products (the rare earths, barium, and strontium) are removed in a reaction layer that forms along the crucible walls. The noble fission products, such as ruthenium, rhodium, palladium, and molybdenum, are not removed, and their concentrations reach equilibrium values that depend on the percentage of fresh material added per pass to replace losses or metal deliberately removed. The resulting fuel material containing the noble fission products as alloying agents is called "fissium." Although the composition of fissium may vary, the composition currently in use contains about 5 wt. % of noble metals.

Magnesia and zirconia both have been promising crucible materials for the melt refining operation. However, recent runs in pressed magnesia crucibles have shown wide variations in the extent of cerium removal for reasons that are not known. The superiority of zirconia was recently shown by two laboratory runs made with plutonium-fissium alloy (20 wt. % plutonium, ~5 wt. % noble fission products, remainder uranium) at 1300°C. In one run a pressed, stabilized zirconia crucible was used with a melt time of 120 min; in the second run a pressed magnesia crucible was used with a melt time of 70 min. The dross formation was 2.7 wt. % of the alloy in the case of the zirconia crucible and 10.2 wt. % in the case of the magnesia crucible from which copious fuming of magnesium occurred.

Zirconium oxide is thus emerging as the superior crucible material. It is somewhat more expensive than magnesium oxide but has the advantage that use of it eliminates the fuming of magnesium which occurs with magnesia crucibles. Use of zirconium crucibles does not result in introduction of zirconium into the melt. The oxygen provided for the formation of the rare-earth oxides results in an oxygen-deficient zirconia.

Studies of the melt refining process have been made on a 2-kg scale using fissium to which cerium has been added to a concentration of 0.6 to 1 wt. % as a stand-in for the rare-earth elements. Data were obtained on the yield of purified ingot and on the extent of cerium removal effected under the liquation condition used (see Table III-1). These, in general, show adequate cerium removal in 3 to 5 hr at 1300°C and in about 2 hr at 1400°C. However, yields were somewhat lower for the 1400°C operation.

Table III-1 MELT REFINING OF FISSIUM: EFFECT OF TEMPERATURE AND TIME ON YIELD AND CERIUM REMOVAL*

Liquation temp., °C	Total liquation time, hr	Yield† of purified ingot, %	Cerium removed, %
1300	3	97	92
1300	3	98	‡
1300	3	96	‡
1300	5	97	>99
1300	5	96	99
1300	5	95	90
1400	2	94	90
1400	3	93	>99
1400	3	95	98

*Conditions: dry-pressed zirconia crucible; 2-kg charges of fissium pins.
†On a cerium-free basis.
‡Data not received.

Melt refining studies have recently been extended to the processing of actual EBR-II fuel pins that are 0.14 in. O.D. by about 14 in. long. Cerium was added to the molten fuel alloy at 1200°C to give an initial concentration of 0.7 wt. %, after which the temperature was raised to the desired value (1300 or 1400°C). Table III-2 shows purified ingot yields of 95 per cent in all three runs, the yield being apparently unaffected by variations in liquation time or temperature. Cerium removal varied only between 82 and 88 per cent. The removals at 1400°C are about the same as those previously found with 2-kg charges of massive metal. However, the removal of 82 per cent of the cerium in 5 hr at

1300°C is lower than that previously found with smaller charges of metal (see Table III-1). Additional runs are to be made for further clarification of conditions.

Table III-2 MELT REFINING OF FISSIUM PINS*

Liquation temp., °C	Liquation time, hr	Yield of purified ingot, %	Cerium removed, %
1400	1	95.4	82
1400	2	95.0	88
1300	5	95.1	82

*Conditions: dry-pressed zirconia crucible; 5-kg charges of fissium pins; cerium added at 1200°C.

1. *Zirconium Removal.* Virtually no zirconium removal has been effected in melt refining runs in zirconia or magnesia crucibles. On the basis that some removal is desired, preliminary runs were made in an attempt to remove zirconium by carbide drossing. The use of graphite in some form resulted in some removal of zirconium, but at the expense of ingot yield (see Table III-3).

Table III-3 REMOVAL OF ZIRCONIUM IN CARBIDE MELT REFINING RUNS

Use of graphite	Time, hr	Temp., °C	Initial Zr conc., wt. %	Zr removed, %	Ingot yield, wt. %
None	5	1300	0.23	10	97
Permanent rod	5	1300	0.35	15	96
Graphite rods replaced every 20 min	5	1300	0.18	45	94
Colloidal graphite coating	4	1300	0.2	27	89
Permanent rod	2	1400	0.2	25	83

Several techniques for removal of zirconium have been investigated in the laboratory. In one of these a graphite disk was floated on molten uranium during liquation, and, in another, 3.2 per cent nitrogen was introduced into the furnace atmosphere. By photomicrographic examination carbide or nitride segregation was found to have occurred. The practicability of separation would require tests on a larger scale.

Work on zirconium removal has been stopped, pending receipt of information concerning the radiation stability characteristics of fissium containing zirconium.

2. *Behavior of Short-lived Fission Products.* The first of a series of melt refining experiments carried out on irradiated short-cooled uranium fissium containing a low concentration of fission products has been performed. The purpose of these experiments include (1) determination of the evolution of radioxenon under standard melt refining conditions, (2) the effectiveness of lowering external pressure on the volatilization of iodine, and (3) the fate of short-lived fission elements.

In this first experiment, after liquation for 2 hr at 1300°C, the furnace was pumped out, and the pressure was reduced to less than 1 mm Hg over a period of 1 hr. Very little of the originally contained iodine has been found in the poured ingot, nor was iodine found in the gas samples. However, the water-cooled walls of the furnace which were protected with aluminum foil condensed major quantities of radioiodine. An undetermined fraction remained in the skull. The poured metal and crucible skull each retained something of the order of 2 to 5 per cent of the radioxenon. Further information is to be obtained on the fates of iodine and xenon.

Preliminary results available show the following retention percentages in the poured ingot for short-lived activities: 2.33-day Np^{239}, 100 per cent; 67-hr molybdenum, 99 to 100 per cent; 12.8-day Ba^{140}, less than 1 per cent; 77-hr Te^{132}, 38 per cent; and 7.5-day Ag^{111}, 59 per cent.

3. *Trapping of Volatile Products.* In addition to the noble fission-product gases, xenon and krypton, volatile products that will be evolved during the melt refining step from a 10-kg charge of EBR-II fuel pins consist of an estimated 44 g of sodium (the residual pin coating after pin decladding), 20 g of the fission element cesium, and 3 g of the fission element iodine.

Two methods are being evaluated for the collection of these volatiles. One method, static collection, consists in placing a surface-active sorbent material in a basket above the crucible, using a Fiberfrax gasket to effect a seal. The second method, gas-sweep collection, consists in placing a collector above the crucible, through which an inert gas sweep is maintained to prevent leakage of volatiles through the collector-crucible juncture. The volatiles may be deposited

on a surface-active sorbent material, as in the first method, or condensed in a cold trap.

The surface-active materials, activated carbon, activated alumina, and molecular sieves are particularly efficacious in retaining sodium, even at elevated temperatures. For example, based on the weight of sorbent material, the retentions of sodium at 800°C are around 20 per cent on molecular sieves and activated alumina and 40 per cent on activated charcoal. Bed capacities are substantially higher at lower temperatures. If loaded to these capacities under atmospheric pressure, sodium is largely removed by evacuation to 1 mm pressure, the retention being only 4 to 10 per cent of the bed weight at 600 to 800°C. If initial loading under atmosphere pressure is held to 4 to 10 per cent of the bed weight, then essentially no sodium removal occurs under evacuation to 1 mm pressure. Experiments employing cesium have recently been made. At 600°C and atmospheric pressure, average percentage retentions of cerium were 30, 70, and 140 for activated alumina, molecular sieves, and activated carbon, respectively.

Oxide drossing studies are under way at Atomics International[56,57] using a 0.5 wt. % cerium–uranium alloy. This alloy is being contacted with small oxide bodies of zirconia, alumina, and urania at 1300°C in an argon atmosphere. With urania the reaction layer that formed could be dislodged by stirring.

The solubility of cerium in uranium at 1345°C was found to be 2.2 ± 0.2 wt. %. The diffusion coefficient of cerium in molten uranium was determined at 1170 and 1200°C. The value of this coefficient was 1.0×10^{-4} sq cm/sec.

It is planned to measure the rate of release of radioactive krypton from 10 kg of Hanford fuel during melting and oxide drossing. This krypton may be absorbed directly or from a carrier helium gas on a liquid-nitrogen–cooled silica gel absorber. A vapor-phase chromatograph is being calibrated for use in determining the absorption efficiency and recovery of krypton and xenon.

Progress of Pilot Applications of Melt Refining

Design of the EBR-II fuel processing plant has been under way at the H. K. Ferguson Co. for about four months on the basis of ANL design requirements. The process equipment design and testing is being carried out by ANL. A résumé of this project will be included in the next issue of this Review.

The Pyroprocessing Refabrication Experiment (PRE) is a multikilogram-scale engineering development effort at Atomics International on the remote decontamination and refabrication of spent metallic uranium fuel. Pyrometallurgical methods will be used for remote partial decontamination, re-enrichment, and recasting of fuel slugs. The reconstituted slugs will be remotely fabricated into fuel rods for reirradiation in the Submarine Reactor Experiment (SRE).[56,57]

Fractional Crystallization Processes

Several processes are currently under investigation which involve dissolution of uranium or thorium-uranium alloy in a metal solvent. These include the Hermex process[58] (under development at ORNL) which employs mercury as a uranium solvent, the Pyrozinc process (under development at ANL) which uses zinc as a uranium solvent,[59] and some work at Atomics International.[56,57] In these processes purification mechanisms of gaseous fission-product evolution and oxide drossing of reactive fission products are operative, but in addition to these is the fission-product–uranium separation that results on precipitation from solution of a uranium-solvent metal intermetallic compound. This is separated from the bulk of the solution, and the uranium is subsequently recovered by decomposition of the intermetallic compound and vaporization of the solvent metal. The uranium is then consolidated by melting.

Hermex process runs were made in larger-scale stainless-steel equipment.[3] Decontamination factors (see Table III-4) in the stainless-steel equipment were lower than those in the glass equipment previously reported by approximately a factor of 100. This indicates that the principal decontamination mechanism in the glass equipment was oxide drossing.

Hydriding of a Submarine Thermal Reactor (STR-2) fuel element followed by refluxing with mercury at 356°C and 1 atm pressure or 800°C and 103 atm pressure was not a promising method for extraction of uranium from the fuel element. Molten magnesium degraded a zirconium-uranium alloy, but neither mercury nor dilute nitric acid extracted uranium from the magnesium matrix. Mercury dissolution

of refractory fuel elements does not appear feasible.

The zinc crystallization process has been named the "Pyrozinc process." It involves the dissolving of metallic fissile materials in zinc at an elevated temperature, cooling to precipitate an intermetallic compound, separation of the intermetallic by filtration or some other suitable procedure, and recovery of the product metal by vaporization of the zinc.

In connection with the fractional crystallization of fission products from molten metals such as zinc, the solubilities of plutonium and uranium in zinc have been determined at 1000°K for various charge ratios, with results[40] as shown in Table III-5.

Table III-5 SOLUBILITY[40] OF PLUTONIUM AND URANIUM IN ZINC AT 1000°K

Charge ratio, Pu:U	Solubility, wt. % Plutonium	Uranium
Pure Pu	2.15 ± 0.15	0
3:1	2.20 ± 0.15	0.40 ± 0.05
1:1	2.10 ± 0.15	0.45 ± 0.05
1:4	1.22 ± 0.10	1.05 ± 0.10
Pure U	0	1.85 ± 0.15

Studies are now under way to develop this process both as an auxiliary for the melt refining process and as a separate and complete process. As an auxiliary process it would be used to process crucible residues and deliberately removed fuel material (drag-out), to provide the separation from noble fission products not effected by melt refining, and also to enable the recovery of fissile material contained in crucible residues.

Data for fractional crystallization of dissolved fissium in zinc have previously shown adequate separation from all noble fission products except ruthenium. On slow cooling, virtually no separation from ruthenium was effected. However, fast cooling has been found to be beneficial in keeping ruthenium in solution from which UZn_9 crystallizes. For example, 47 per cent of the ruthenium remained in solution while crystallizing out 96 per cent of the uranium by cooling from 720 to 500°C. Separation may be increased by countercurrent fractional crystallization techniques.

Table III-4 REMOVAL OF FISSION PRODUCTS FROM IRRADIATED URANIUM* BY HERMEX PROCESS[3]

Component	Removal, % of total: Dissolving and slagging, including hot filtration	Filtration, including cold filtration after recrystallization	Aqueous washing, agitation of quasi-amalgam with cold 1N HCl	Over-all, including experimental handling
U (losses)	5.12	0.474	0.417	6.47
Hg (losses)	32.0			16.0†
Gross gamma	55.7	6.8	1.32	67.2
Gross beta	29.0	1.9	1.62	31.5
Cs beta	56.5	3.57	1.21	73.5
Sr beta	32.8	0.88	2.63	40.2
Total rare-earth beta	16.0		1.77	23.0
Ru beta	25.0	1.87	3.28	36.6
Zr, Nb gamma	59.8	0.62	0.77	68.3
Pu alpha	4.2		1.1	64.5

*Uranium irradiated at 3.6×10^{17} neutrons/sq cm, decayed 3.5 years.
†Inadequate condenser on dissolver.

An active run employing the Pyrozinc process was made to ascertain the general behavior of fission products present in trace concentrations. In general, decontamination was relatively low, 30 to 60 per cent of fission products such as the rare earths, zirconium, and niobium being removed (see Table III-6). Ruthenium was well separated, only 2 per cent accompanying the uranium. This preliminary experiment indicates a large coprecipitation effect.

Systematic laboratory studies of coprecipitation of trace activities have been started. The use of rapid rather than slow cooling appears to decrease coprecipitation.

The solubility of lanthanum in zinc was determined. The results show it to be more soluble than cerium and to have approximately the same

heat of solution. The eutectic occurs very near the freezing point of pure zinc.

Engineering problems encountered in the Pyrozinc process are the following:

1. Separation of insoluble material from a solution of uranium in zinc at a temperature of 700 to 800°C.

2. Separation, at a temperature of 500°C, of UZn_9 by vaporization of the zinc. Filtration has been employed to date for the first two separations, but other solid-liquid separation procedures will also be investigated. No difficulty has been encountered with the low-temperature filtration, but the high-temperature filtration has been troublesome because of plugging of vent lines with condensed zinc. By use of zinc vapor traps, successful high-temperature filtrations of 5 kg of zinc-uranium solutions have been made.

3. Recovery of uranium from UZn_9. This has been demonstrated on a small scale. A uranium button (~70 g) containing about 30 ppm of zinc was produced.

A series of liquid-metal extraction experiments are also in progress at Atomics International to study the decontamination of irradiated thorium-uranium alloy by dissolution in molten zinc followed by fractional crystallization. Irradiated thorium-uranium alloy was dissolved in molten zinc at 700°C. As the melt was cooled slowly from 830 to 440°C, samples were taken to determine fission-product distribution and solubilities at elevated temperatures for thorium and uranium in zinc in the presence of each other.

High-temperature separations methods for uranium oxide fuels are also under investigation. An electrolytic cell employing a fused halide salt bath and a molten zinc cathode has been assembled for uranium dioxide purification. In a preliminary test uranium was deposited in zinc solution. A search is being made for halide mixtures that melt below 600°C to avoid excessive zinc vaporization.

Another proposed approach involves reduction of uranium dioxide by magnesium in zinc solution followed by reoxidation of the uranium with zinc oxide. The fission products are expected to remain in zinc solution or in a dross produced on initial solution of the uranium.

Table III-6 DISTRIBUTION OF ACTIVITY* IN PRODUCT PHASES (PYROZINC PROCESS)[40]

	Activity, % of total accounted for								
Products	Pu	β	γ	Zr	Nb	TRE	Sr	Ru	Cs
Filtrate at 500°C	10.27	11.96	23.44	38.90	9.13	4.11	1.52	94.12	15.65
Wash soln.	2.20	0.86	2.80	3.73	3.02	0.42	0.43	3.49	1.40
UZn_9 filter cake	83.30	60.13	37.46	31.35	40.25	70.79	18.73	2.02	18.48
Dross	4.23	27.15	36.30	26.02	47.60	24.68	79.32	0.37	64.47

*Tracer fission-product concentrations.

Electrorefining Processes for Fuel Purification and Recovery

As reported in Vol. 1, No. 1, of this Review, work on electrorefining at Knolls Atomic Power Laboratory (KAPL) was terminated because of changes in the program. A terminal report of this work which had been issued was discussed. In the last period several additional topical reports were issued. A method is described for recovering uranium from the fused-salt bath employed as the electrolyte in the electrolysis cell which must be periodically discarded.[60] An electrolytic process is used in which the uranium is deposited as a dendritic deposit at the cathode. This dendritic deposit is then subsequently recycled to the electrorefining cell. Background laboratory work conducted for the production of uranium by electrolytic reduction of uranium oxides in fused-salt electrolytes is also reported.[61] The electrolytic cell was operated at temperatures above the melting point of uranium. The effects of current, salt-bath composition, and other variables on efficiency and cell operations are discussed.

The rapid settling of the oxide feed in the KAPL process for electrowinning uranium from its oxides causes operating trouble. The oxide settling problem manifests itself in two ways. First, the oxide leaves the region of the anodes that are suspended in the cell, and these electrodes then become badly polarized. Second, the oxide settles out as a dense sludge on the

bottom of the cell which serves as the cathode. This sludge interferes with the agglomeration of the molten product metal into compact oxide free masses. As a result stringers and beads of metal form in the oxide sludge, and eventually a short circuit develops between the electrodes.

The possibility of making use of the anodically generated gases to stir the bath is considered as a means of overcoming the settling problem.[62] The combined suspension of uranium dioxide powder was studied using pseudoelectrodes and an argon sparge gas. This work permitted only a general examination of some of the cell variables effecting stirring, but it was considered that it should be possible to overcome the oxide settling problem in a production cell by controlling the oxide particle size and by optimizing the stirring efficiency by the anode gases.

Thorium was successfully electrolyzed at Atomics International[56,57] using thorium as the anode and iron as the cathode. The temperature was held at 1050°C. A thorium-iron alloy formed at the cathode and dripped off. Thorium was also successfully electrolyzed into a molten zinc cathode, giving a thorium concentration in zinc of 4.5 wt. % at 620°C and 15.5 wt. % at 706°C. At the lower temperature graphite can be used as a container.

Pyrometallurgical Processing of Plutonium-rich Fuels

The investigation of pyrometallurgical methods for the purification of plutonium-cobalt and plutonium-iron fuels is under way at Los Alamos Scientific Laboratory (LASL).[63] The experiments now being done are exploratory work (~100 g scale), and those methods that show promise will later be scaled up to about 1 kg. Oxidative slagging appears to be an effective method for removing essentially all the rare-earth fission-product elements, whereas zirconium, molybdenum, and ruthenium concentrations are not seriously affected. Other methods, such as liquation, fluoride and carbide slagging, liquid-metal extraction, and various fused-salt systems, are also being studied. Although carbide slagging serves to remove zirconium, a large amount of plutonium carbide is also formed, and for this reason carbide slagging is not considered a promising pyrometallurgical method for a concentrated plutonium fuel.

Zirconium, molybdenum, and lanthanum are believed to be removable from rich plutonium fissium alloys by virtue of limited solubilities. Filtration of a liquid phase containing initially 1.8 wt. % lanthanum, 0.90 wt. % zirconium, and 0.75 wt. % molybdenum showed concentrations of 0.28, 0.56, and 0.56 wt. %, respectively, in the liquid. The method thus has some promise for the removal of these fission elements.

Preliminary electrolysis experiments using tantalum and plutonium anodes and iron cathodes have been conducted.[64] The electrolyte was a eutectic mixture of lithium and potassium chlorides. The results indicate that plutonium chloride and the alkaline chloride decomposition potentials are sufficiently different to permit selective deposition of plutonium on the iron cathode.

The usefulness of a calcium-magnesium eutectic alloy as an extractant for fission products is being tested. The mutual solubility of components of the immiscible phases in each other was determined by contacting the eutectic alloys with the 9.5 at. % iron–plutonium alloy at 600°C for 40 hr. After separation of the phases, the calcium-magnesium phase contained 0.06 wt. % plutonium and 0.19 wt. % iron. These results are favorable, and the use of the eutectic alloy will now be determined as an extractant for fission products from the fissium alloy.

Equipment is being assembled[65] to measure the solubility of plutonium in mercury at temperatures up to 350°C. If the solubility is favorable, the use of mercury as an extractant will be tested with the fissium alloys.

Blanket Processing—Magnesium Extraction

The magnesium extraction process is currently being developed to recover the plutonium bred in natural uranium or depleted uranium blankets. The initial application will be for recovery of plutonium bred in the blanket of the EBR-II reactor. One version of the process consists in successive liquid-liquid batch extractions of plutonium from a 5 wt. % chromium–1 wt. % plutonium–uranium alloy into magnesium at a temperature of around 950°C. Subsequently, the plutonium is volatilized, leaving behind a concentrated plutonium-in-uranium product.

Four successive equal-weight extractions were carried out on a uranium phase initially 1 wt. % in plutonium. Plutonium distribution coefficients varied between 0.22 and 0.25 (mole

ratio basis). The plutonium material balance was 92 per cent. The use of graphite as a container material has been ruled out because of excessive reaction with plutonium.

A system of considerable interest for a reactor blanket is the ternary system, magnesium-thorium-uranium, in which U^{233} would be bred.[66] A possible processing method using this ternary is based on the very low solubility of uranium and the very high solubility of thorium in magnesium. Thus, if the magnesium-thorium solution is held quiescent above its melting point, the uranium will settle out in the lower part of the alloy or collect as a separate phase. The solubilities of uranium in these magnesium-thorium alloys have been determined over a range of temperature and composition.

In addition, the formation of thorium hydride from thorium in solution causes the precipitation of the thorium. Since this reaction might bind application in a pyrometallurgical process, the solubility of thorium hydride in magnesium was determined over a range of temperatures. Solubility increased from 8.1 wt. % at 675°C to 25 per cent at 800°C at 1 atm hydrogen.

Container Materials Research

Container materials are being tested and developed at Ames, Iowa, for potential liquid-metal reactor fuels, blankets, and coolants. Container metals that are promising in static corrosion tests are fabricated into loops in which long-term corrosion behavior under dynamic conditions is ascertained. Among the container materials under investigation are tantalum, vanadium-chromium and vanadium-tantalum alloys, yttrium, yttrium-titanium and yttrium-columbium alloys, silver, and Inconel.

1. *Loop Tests.* Long-term corrosion tests in tantalum are presented in Table III-7. No attack or mass transfer corrosion of tantalum occurred on circulation of magnesium–35 wt. % thorium or bismuth–5 wt. % uranium alloys. The addition of 0.3 wt. % magnesium to the uranium-bismuth alloy produced some slight attack, and the test was subsequently stopped. Sodium is presently being circulated in an Inconel loop.

In these loops a high-temperature linear magnetic pump, of which there is no commercial counterpart, pumps the molten alloys at up to 5 gal/min at 1000°C. A heating transformer provides the necessary heating to maintain temperatures of around 1000°C. The Δt around the loop is around 100°C.

It was found that Inconel is the best material to use as a protective envelope for tantalum since diffusion of nitrogen and oxygen, which causes tantalum embrittlement, is lower than that for stainless steel. The annulus between the tantalum and stainless steel is filled with helium.

2. *Yttrium as a Container Material.* Recently, considerable interest has developed in yttrium and yttrium alloys as container metals. The yttrium must be protected from air oxidation by a backing metal. A problem exists in the selection of an outer jacket material because yttrium reacts with nickel even if present in very small concentrations. Type AISI 446 steel looks promising.

Results of static corrosion tests using yttrium are (1) yttrium was dissolved to a depth of 40 mils by a thorium-uranium-aluminum alloy held at 700°C for 1000 hr, (2) no attack occurred by a uranium-chromium eutectic alloy held at 900°C for 800 hr, and (3) a 5 wt. % uranium–bismuth alloy has been successfully held for around 1000 hr at 900°C.

3. *Other Container Material Tests.* A dynamic corrosion test of the uranium-iron eutectic in a silver tube backed by tantalum indicated little or no corrosion in 100 hr. The system consisted of a sealed tube (ends heated to 835 and 900°C) which was partially filled with the alloy and rocked to test dynamic corrosion.

Table III-7 CIRCULATING METAL ALLOY CORROSION TESTS IN TANTALUM*

System	Temp., °C	Time, hr	Ta corrosion
Mg–35 wt. % Th	800	2000	None detectable
Bi–5 wt. % U	950	5250	None detectable
Bi–5 wt. % U–0.3 wt. % Mn	950	4500	Slight attack†

*Data from Ames Laboratory, Iowa State College.

†Since manganese lowered the melting point by only 30°C, work with this ternary was stopped.

The long-term interaction between graphite and molten uranium was studied[67] in the temperature range 1150 to 1400°C. Preliminary results indicate that a protective, adherent coating forms at a rate that is strongly dependent on temperature.

Miscellaneous

1. *De Boer Iodide Process.* Experiments were reported on the use of the de Boer volatile iodide process as a method for decontamination of uranium metal or uranium alloy fuel elements.[68] Decontamination from all long-lived radioactive fission products except zirconium was obtained by forming uranium tetraiodide, volatilizing the iodide, and then decomposing it to deposit uranium metal on a hot wire. By selective condensation of the uranium tetraiodide, separation of uranium and zirconium was produced.

The ability to codeposit uranium and zirconium, as might be desired in reprocessing uranium-zirconium fuel elements, was demonstrated. The deposition of molten uranium metal on a heated zirconium carbide cylinder and the continuous removal of the uranium from the cylinder were also investigated.

A design of a processing plant is described, and the problems inherent to its construction and operation are discussed.

2. *Uranium–Nobel Metal Equilibrium Diagrams.* Equilibrium diagrams of uranium-ruthenium, uranium-rhodium, and uranium-palladium systems are being studied at the National Bureau of Standards (NBS).[69] Uranium-ruthenium diagrams are now being studied in the range of 75 to 100 at. % ruthenium. In the uranium-rhodium phase diagram a eutectic has been found to exist at a rhodium concentration of 12.2 wt. %, which has a melting point of 870°C. Two intermetallic compounds, UPd and UPd_3, have been postulated to exist in the uranium-palladium phase diagram. Another compound, U_2Pd_3, is suspected. These phase-diagram studies are continuing.

3. *Fission-product Volatilization Studies.* The release of fission products on melting of various types of fuel elements in an inert atmosphere or in the presence of air or steam was studied by Parker and Creek[70] to provide information for reactor safeguard considerations. The important fission products released were the rare gases, iodine, and cesium. The percentage release of fission products to the atmosphere from a molten reactor fuel is apparently proportional to the melting temperature and is affected mainly by the degree of oxidation, the concentration of fission products, and the type of fuel. Lesser factors are the nature of the surrounding atmosphere, size of sample, the degree of subdivision of fuel particles, and time at temperature. A zirconium alloy of the STR type, after a burn-up of 15 per cent when melted at 1850°C, released up to 95 per cent of the rare gases, 80 per cent of the cesium, 60 per cent of the iodine, and only a trace of strontium. An aluminum alloy of the MTR type containing trace concentrations of fission products upon melting at 700°C released only 2 per cent of the iodine, 10 per cent of the rare gases, and negligible portions of other fission products.

The removal of the fission product xenon by transient (or zone) melting was studied by Gilman[71] to determine the xenon that could be removed on rapid movement of a molten zone through a fuel element. Solution of cladding materials would be minimized by such a procedure. Xenon (synthetically introduced through decay of I^{131}) was essentially completely removed by one pass (3 to 5 m/min) under vacuum.

4. *Processes for Thorium-Uranium Alloys.* Fission-product vaporization which occurs during slow drip melting under high vacuum of thorium–3 wt. % uranium alloy is being investigated at Atomics International.[56] Drip melting of a lightly irradiated alloy showed no loss of uranium and thorium, only slight removal of protactinium, and 11 per cent removal of rare earths. Small-scale studies were completed on removal of fission products by nonconsumable arc melting.

Table III-8 PROTACTINIUM EVAPORATION FROM THORIUM BY ARC MELTING[57]

Run	Time, min	Weight, g	Temp., °C	Pa removed, %
15	4	3.29	1950	4.3
16	4	3.64	1950	41
17	8	4.17	1900	30
18	10	4.20	1700	7.5

The last series of experiments were undertaken to determine protactinium behavior. Results in Table III-8 show that protactinium is difficult to remove, requiring long heating at a high temperature (1950°C for 8 hr).

Corrosion

Corrosion is a subject that is an integral part of each process development program. Because

it is a problem that lends itself to setting up specific programs, much of the literature is reported under this specific heading. In this section an attempt will be made to cover progress on programs that have been set up to cover specific corrosion problems in a systematic way.

Solvent Extraction

Various aqueous head-end treatments are being devised by different sites that will make present solvent-extraction equipment usable for processing some of the more recent fuel-element types. A number of these have corrosion problems such that the selection of materials of construction is not obvious or where limitations of materials need to be clarified.

1. *Zircex.* The Zircex process is directed toward the disintegration and dissolution of zirconium matrix fuels by high-temperature (600°C) gas-phase hydrochlorination followed by nitric acid treatment to solubilize residues. Promising materials (see Vol. 1, No. 1, p. 63, this Review) were alternately exposed[3] to gaseous hydrogen chloride at 600°C for 11 hr and to boiling nitric acid (containing UO_2Cl_2) for 2 hr. After 25 cycles Haynes 25 and S-816 appeared to be the best. Tantalum and titanium failed in the hydrogen chloride portion of the cycle. Other alloys tested that were not satisfactory were Inconel, Hastelloy B, Hastelloy C, Haynes 21, S-590, Carpenter 20, and Illium R. Further cyclic testing revealed intergranular attack in S-816 alloy of 2 to 14 mils/month (rate was influenced by nitric acid concentration and chloride ion content of dissolver solution); rates of attack on Haynes 25 were 2 to 4 mils/month with acid content held below 5*M* (rate appeared independent of chloride ion concentration).[T2] Haynes 25 is the present qualified choice.

Liquid-phase hydrochlorination is also being considered for Zircex. Seven-day corrosion tests of five alloys were made in boiling aluminum chloride–ammonium chloride sparged with hydrogen chloride.[T2] Molybdenum, nickel, and Hastelloy X had rates of attack that appear low enough to be promising, whereas Hastelloy C and Nichrome V were not far behind (6 to 8 mils/month).

2. *Darex.* Darex is directed toward the dissolution of stainless-steel matrix fuels by dilute aqua regia. Dissolution is followed by chloride stripping, feed adjustment, and introduction into a solvent-extraction plant. Studies on titanium as a dissolver material have continued.[3] In prolonged tests (1500 hr) in boiling 2*M* hydrochloric acid–5*M* nitric acid, rates of attack were initially 1 mil/month and decreased with time as corrosion products accumulated. The presence of ruthenium decreased the rate by a factor of 4 to 10. During dissolution of stainless steel, the rate reached a maximum of 0.03 mil/month after 1500 hr. Haynes 21 alloy had comparable initial corrosion rates, but these did not decrease with time.

Tantalum and titanium were tested with dissolution potentials applied to them.[3] The former embrittled, probably because of hydride formation; the latter did not. Because of this hydride formation, tantalum, although compatible chemically, appears to have limited usefulness as a dissolver material.

The effect of temperature on corrosion of titanium and tantalum in 2*M* hydrochloric acid–5*M* nitric acid was determined.[5] The corrosion rate of titanium increased by a factor of 6 when the temperature was increased from 115 to 145°C. No corrosion was detected in any of the tantalum tests.

A pilot plant for the Darex process has been designed and is being built.[T3] The dissolver, condenser, and acid receiver will be made of titanium.

The problem of stripping chloride from dissolver solutions is common to both the Darex and Zircex processes. Under stripping conditions (not defined) tantalum corrosion rates were negligible; titanium rates were low in the liquid phase and at the interface, and the titanium rate was 0.6 mil/month in the vapor phase.[3] The latter figure is dependent on the presence of nitrogen dioxide, nitrosylchloride, or chloride. In the liquid phase the presence of nitric acid, uranyl ion, and stainless-steel dissolution products inhibits corrosion.

Type 304L stainless steel was tested in boiling synthetic feed (dissolver solution that had been stripped of chloride and concentration adjustments made).[T4] In 1*M* uranyl nitrate, 0.15*M* nitric acid, 40 g/liter dissolved stainless steel, and no chloride ion, liquid-phase corrosion was 3 mils/month. Chloride ion up to 0.01*M* had no significant effect, tripling the chromium content doubled the rate, and eliminating the nitric acid halved the rate. All liquid-phase samples were attacked intergranularly; vapor-phase corrosion

was low. Rates of attack on titanium under the same condition were below the limits of detection.

3. *Zirflex.* Another process being studied is the chemical decladding of Zircaloy-2–clad uranium cylinders with modified or unmodified 6*M* ammonium fluoride, followed by core dissolution in a nitric acid medium. Corrosion information is available for both process steps.[5,73,74]

Type 304L stainless steel that had been previously attacked intergranularly by boiling 65 per cent nitric acid was exposed to boiling 6*M* ammonium fluoride and 0.95*M* ammonium zirconium fluoride–0.3*M* ammonium fluoride.[73] Corrosion rates were less than 0.1 mil/month Exposure to 3*M* ammonium fluoride–3*M* hydrofluoric acid resulted in attack as high as 8 mils/month.[5] Ammonium nitrate additions (considered for dissolving the tin in the Zircaloy) had little effect. Other experiments conducted in various boiling mixtures of ammonium fluoride and ammonium zirconium fluoride indicated rates of less than 0.05 mil/month.[74] Titanium corroded rapidly in these solutions.[73] Haynes 25 appears promising.[73]

The 18-8 stainless steels appear to be useful in the nitrate dissolution although they are sensitive to fluoride ions. Added aluminum complexes fluoride, and, if the aluminum to fluorine ratio is kept above 6, rates of attack on sensitized types 347 and 316 do not exceed 1 mil/month in boiling solution.[5] In the absence of aluminum ions titanium appears to be more sensitive to fluoride than the stainless steels.[74] Haynes 25 was tested in typical boiling dissolver solutions (12*M* nitric acid, 10*M* nitric acid–0.3*M* uranyl nitrate, 6*M* nitric acid–1.0*M* uranyl nitrate), and in no case did corrosion exceed 4 mils/month.[73]

Haynes 25 was cycled in 6*M* ammonium fluoride and 12*M* nitric acid (24 hr each). No attack was observed in the former; 4 mils/month was observed in the latter.[73]

4. *Sulfex.* The Sulfex process has been devised to declad stainless-steel fuels with dilute sulfuric acid. A desirable goal would be to find a material of construction that is compatible with both the Sulfex and Zirflex processes. It is thought that Carpenter 20 might be such a material.[5] Tests of Carpenter 20 under Sulfex process conditions (6*M* sulfuric acid) require further clarification. In glass-capsule tests rates[73] were found to be 1 to 2 mils/month at 125°C and 7 to 120 mils/month at 145°C. The rates seemed to be independent of dissolved stainless steel and phosphates. In boiling Hewey type tests* in the same solution, corrosion was reduced from 80 to 2 mils/month by the addition of 56 g/liter of dissolved corrosion product. Haynes 25 failed rapidly in boiling 6*M* sulfuric acid.

5. *Miscellaneous Aqueous Corrosion.* Experiments are being performed on the effect of halogen ion contamination of boiling nitric acids on the corrosion of type 304L stainless steel.[72] Preliminary tolerance values of chloride ion reported range from 0.1 per cent for 45 per cent nitric acid to 0.5 per cent for 18 per cent nitric acid.

Of general interest is a corrosion bibliography recently published that supplements Corrosion: A Bibliography of Classified Report Literature, TID-3047, and Corrosion: A Bibliography of Unclassified Report Literature, TID-3048, in the area of aqueous corrosion.[75] The document includes references to June 1, 1957.

A recent publication on the adverse behavior of titanium and its alloys has been released.[76]

Fused-salt Volatility Process

This process is directed toward the economic processing of zirconium matrix fuels. The fuel assemblies are dissolved by hydrofluorinating in a fused-fluoride medium; uranium hexafluoride is recovered by fluorinating the dissolved uranium tetrafluoride.

Graphite is one of the promising materials of construction for the hydrofluorination portion of the process. Further tests with National Carbon Co. type CS graphite and an experimental impregnated grade from the same organization (molded ATL base stock given six impregnation treatments) verify that dimensional changes do not exceed 3 mils/month.[44] The tests were conducted in equimolar sodium fluoride–zirconium fluoride at 600°C for periods in excess of 1000 hr. No interface or gas impingement effects were observed.

Lathe turnings were taken from the impregnated graphite corrosion tested above. These were analyzed spectrochemically to determine salt penetration. The data indicate that penetration was very slight.[44]

*Boiling Nitric Acid Test for Corrosion-resisting Materials, ASTM designation: A262-52T.

A large CS graphite crucible (1½ in. wall) containing the same fused-fluoride mixture was thermally cycled forty times between 600 and 180°C to induce possible damage by salt permeation followed by freezing and thawing action.[44] Spectrochemical analysis revealed salt penetration to a depth of 500 mils, but no mechanical degradation of the graphite was observed.

Of the metals, nickel and nickel alloys appear the most promising for the hydrofluorination step. Hastelloy W (23 to 27 wt. % molybdenum, 6 wt. % chromium, 4 to 7 wt. % iron, balance nickel) was tested for 250 hr in fused sodium fluoride–zirconium fluoride at 650°C and showed a slight weight gain. Slight intergranular attack was evident near the surface. INOR-8 (10 to 20 wt. % molybdenum, 5 to 10 wt. % chromium, 4 to 10 wt. % iron, balance nickel), an experimental nickel-molybdenum alloy, exposed to the same environment corroded at the rate of 0.09 mil/month, and A-nickel corroded at 8.9 mils/month.[72] Additional exposures of the nickel-molybdenum alloys are contemplated in order to determine the effect of further carbon precipitation on susceptibility to intergranular attack.

A study was reported recently on radiation effects on Inconel in molten fluoride environments (hydrogen fluoride was not a part of the studied environment).[77] Among the factors observed were the corrosion of Inconel and the physical and chemical properties of the fluoride melts. The tests were conducted in three in-pile loops in the Low Intensity Test Reactor (LITR). No changes in the above factors occurred.

A tracer technique in the study of corrosion of Inconel in fused-fluoride salts was utilized to characterize mass transport and diffusion of chromium in the metal.[78] It was found that grain-boundary diffusion was more rapid than volume or transgranular diffusion.

Pyrometallurgical Processes

Current corrosion information available related to pyrometallurgical separations includes studies on materials to hold molten uranium, thorium, magnesium, uranium-bismuth, zinc, and plutonium.

A basic approach to the corrosion of ceramic oxide crucibles by molten uranium was made.[79] Dense, high-purity alumina, magnesia, zirconia, beryllia, and thoria were used. Wettability of the oxides via measurements of contact angles of sessile drops on polished oxides was determined. All combinations of alloys and oxides were found to be nonwetting except 4 per cent molybdenum–uranium alloy and 4.6 per cent ruthenium–uranium alloy on alumina.

Corrosion of the ceramics can be calculated from the rate of melt contamination. For alumina the rate of contamination of uranium by aluminum was 13 mg/(sq cm)(hr) at 1330°C; for beryllia, 0.040 mg beryllium/(sq cm)(hr) at 1330°C; for thoria, 0.016 mg thorium/(sq cm)(hr) at 1300°C. Rate of attack of alumina increased eightfold when temperature was increased from 1200 to 1330°C. The effect of uranium alloying agents was also studied.

Molten uranium–5 per cent chromium alloys[80] were successfully held in preoxidized crucibles of uranium–10 per cent niobium at temperatures of 860 to 950°C. It was found that thermal cycling tended to break down the protective oxide layer.

Yttrium has been found to be reasonably resistant to molten uranium.[81] Alloys with titanium and niobium are being considered for further tests. It has been suggested that, because of the immiscibility of uranium and silver, the latter may be useful for holding a uranium-iron eutectic at 900°C.

Of interest is a study of refractories that has been made in connection with uranium reduction.[82] Of those tested, magnesia appears the most promising. It was resistant to both sodium fluoride and uranium at 2200°F in short-term tests. At higher temperatures it was attacked by aluminum fluoride, magnesium fluoride, calcium fluoride, and uranium. Materials considered unsuitable include alumina, zirconia, and mullite.

Thorium-magnesium eutectic was circulated for 2000 hr in a tantalum loop with cold and hot leg temperatures of 900 and 1000°C, respectively.[81] No localized attack or mass transfer was observed. Circulation of 5 per cent uranium in bismuth for 5200 hr at 900 and 1050°C produced no observable attack in tantalum. Addition of 0.3 per cent manganese to the environment did produce some attack in 4500 hr at 900°C.

Reactor corrosion studies of molten plutonium presently being investigated could be useful in pyrometallurgical processing.[83] Refractory metals have been used with measurable success. Tungsten and tantalum are somewhat better than molybdenum and niobium. Static tests with tantalum have been run successfully for 9000 hr at 650°C.

A corrosion problem associated with the uranium-zinc fractional crystallization process is the selection of a material of construction for zinc. Aluminum (½ per cent) was added to zinc in order to determine its effect as an inhibitor in Armco iron.[44] The exposure was for 27 hr at 700°C; moderate attack was observed. Similar results were obtained with Armco iron sprayed with aluminum.

Homogeneous Reactor Processing

A general description of the chemical processing of the aqueous fuel from the Homogeneous Reactor Test (HRT) has recently been published.[84] The processing plant installed as an integral part of the reactor installation was recently modified by incorporation of a tantalum-lined dissolver and decay storage tanks.[3] Additional tests in a high-pressure loop have been made.

The reactor fluid is drawn off in a small side stream, and solids are separated in dual hydroclones. Two core fluid processes are considered for the hydroclone underflow: (1) combination with thorium oxide blanket slurry, evaporation for heavy-water recovery, dissolution in nitric acid, and solvent-extraction separation, and (2) separation of solids from supernatant, peroxide precipitation of uranium from the latter, and dissolution and reconstitution into fuel. The second process is receiving the greater consideration.

The hydroclone retains its role as primary separation device for insoluble fission and corrosion products in either process. Recent articles on the design of such units have appeared.[85,86] Corrosion of titanium hydroclones in uranyl sulfate solutions at 250 to 300°C is reported to be 10 mils/year. Various tests have been made to determine the efficiency in removing synthetic corrosion products, fission products, and zirconium oxide (PuO_2 substitute) from slurries.[83,84,87] The tests have been complicated by the tendency of solids to become adsorbed on vessel walls. Efficiencies of 10 to 25 per cent have been reported. Solids concentrations that are 10 to 1000 times greater than those in the main stream have been achieved in the underflow pot. A concentration factor of 30 is considered adequate for poison removal from the core fluid.

Peroxide precipitation of uranium from the underflow pot supernatant has been done most successfully with 2 per cent sodium peroxide. Resulting decontamination from cesium is greater at lower uranium concentrations, being 50 and 2 at 5 and 150 g uranium/liter, respectively.[88] A decontamination factor of 30 is probably acceptable.

Uranium losses during precipitation, settling, and washing were found to be lower at 2°C than at 40°C; precipitates were also denser and settled faster.[89]

Work reported on the processing of uranyl sulfate blanket solutions has been restricted to the behavior of plutonium. Absorption of plutonium on vessel walls such as occurred in a LITR irradiation in titanium at 250°C appears to be real and serious.[87,89] Valence states of plutonium in these solutions is also being investigated.[84] A method for processing thorium oxide blanket slurries that appears promising consists in co-slurrying the thorium oxide with litharge.[87] Uranium, cesium, and neodymium selectively adsorb on the litharge. Cesium, previously adsorbed on thoria, is desorbed by co-slurrying with litharge at 250°C.

The behavior of iodine and the noble gases is also being studied. In the HRT mock-up iodine was found to move rapidly from the high-pressure system to the low-pressure system. Removal of iodine with silver-alundum beds has been found to be more complete at 150 than at 120°C; silver-plated Yorkmesh is also effective.

Noble gases are to be removed by charcoal beds. Xenon adsorbs more readily than krypton.[87] Moisture in the charcoal reduces its capacity for the noble gases by 25 per cent. Molecular sieves have also been considered as an adsorbing material. The two charcoal beds from the Homogeneous Reactor Experiment (HRE) were studied to determine the distribution of xenon and krypton daughter activities: Y^{90}, Cs^{137}, Sr^{89}, and Sr^{90}. It was evident from the distribution patterns that considerable channeling had occurred during reactor operation.[89]

The Liquid Metal Fuel Reactor (LMFR) concept is undergoing extensive development because of its promise as a power reactor capable of thermal breeding by the thorium cycle. A preliminary design of a 550-Mw power plant has been presented by a BNL industrial study group.[90] The liquid bismuth fuel and blanket offer the possibility of continuous processing by non-aqueous methods such as volatility or pyro-

chemical techniques. The AEC LMFR experiment is being carried forward under the direction of the Babcock & Wilcox Co., and detailed plans have been published.[91,92] Alternate chemical process schemes are being considered at present.

Major development of the LMFR concept has been done at BNL over the past several years. The work on the BNL process for extraction of fission-product poisons from core fuel with fused chlorides has been largely summarized.[93,94] Recently a study of alternate chemical processing schemes has been undertaken at ANL.[40] Fused-salt volatility processes previously studied in connection with STR fuel processing may be used.

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Survey of Existing Problems

During this quarter the AEC issued a report[1] covering the current status of waste disposal problems.

High-level wastes result from the chemical processing of irradiated reactor fuels and are evolved primarily at HAPO, Savannah River, and the National Reactor Testing Station (NRTS). Table IV-1 lists pertinent factors that measure the magnitude of the high-level liquid waste storage situation. The cost figures cited are felt to be conservative since the cost of process equipment (e.g., evaporators) and facilities in which both waste streams and product streams were treated is not included. The differences in cost per gallon at various sites are striking and are influenced by many factors such as size, materials of construction, and philosophy of operation. It is interesting to note that at HAPO (where costs for tankage alone of ~30 cents per gallon have been realized), the estimated cost for additional tankage to 1957 is 77 cents per gallon.

Low- or intermediate-level liquid wastes result from fuel processing operations also, usually from second- and third-cycle separations, and from fuel dejacketing. In addition, they result from reactor cooling systems and laboratory and laundry operations. In proper environmental situations these wastes are susceptible to direct dispersal to the environment or to discharge following treatment. Because of the large volume of wastes, millions of gallons per day, total costs of treatment where required tend to be substantial. A summary of low-level liquid waste discharged and associated operating costs is given in reference 1. The major operation of this kind is at HAPO and is related directly to the environmental situation existing there. Approximately 50,000 curies/month is discharged at HAPO, and this is expected to continue. Since strontium and cesium have been scavenged from this activity, it essentially consists of short-lived material when discharged. Nitrate ion and ruthenium, and more recently Co^{60}, have been detected in monitoring wells associated with these operations but not at health-significant levels to date.

Table IV-1 HIGH-LEVEL LIQUID WASTE HANDLING DATA*

	HAPO	SRP	NRTS	Total
Wastes in storage 10^6 gal	58.2	3.5	0.38	62.08
Total tank capacity, 10^6 gal	90	12.2	1.6	103.8
Total No. of tanks	145	16	9	170
Cost (tanks and appurtenances), $\$10^6$	37.5	16.6	6.6	60.7
Cost, \$/gal capacity	0.41	1.36	4.10	5.87
Estimated tank operating costs, \$/year	50,000			
Future Estimates† (to June 1959)				
Additional wastes, 10^6 gal	9.1		1.5	
Additional cost, $\$10^6$	7		6.5	
Additional cost, \$/gal capacity	0.77		4.30	

* Includes data up to Jan. 1, 1957.

† At HAPO, if present plans for scavenging cesium and strontium and discharge of supernatants to soils are successful, it is likely that the volume of waste in storage will not increase over present levels and the need for additional tankage may be reduced or eliminated. Savannah River future tank requirements, dependent upon operating plans for SRP reactors, are not included. The installation of a waste disposal development facility at NRTS is estimated to be completed in 1959. In this facility, the first prototype of its kind, it is proposed that high-activity wastes containing high concentrations of aluminum nitrate will be converted to oxides (as an initial step in an ultimate disposal scheme). Since the successful operation of this facility will dictate future waste storage requirements, longer-term estimates do not appear warranted.

Operating Experience

Some good information[2] has become available from HAPO on temperature gradients in the walls of waste storage tanks. Temperature gradients are presented as a function of time,

location, and filling procedures. The temperature gradients calculated range from 6 to 109 °F/ft. The rate of heat transfer to the ground from a million-gallon tank has been found to be about 2×10^5 Btu/hr after boiling has been established for several months. The value goes through a maximum that may be as high as 10^6 Btu/hr just as boiling begins. In some cases secondary gradient maximums are found at times well after the start of boiling. These occur at places where the wall previously immersed in 212°F steam is suddenly exposed to the higher temperature of waste solution as the liquid level rises. It was noted that, the more concentrated the waste with respect to fission products, the more severe the temperature gradients.

In the recommendations it is suggested that dilution of wastes to the point where ultimate tank capacity will not be impaired be used as a technique to minimize temperature gradients in waste tank walls. It is also recommended that the practicability of using an insulating layer of air or fractile grout between the steel tank liner and the concrete walls be studied as a means to minimize tank wall temperatures and temperature gradients in future tank designs.

Seepage pits have been used as a method for disposing large volumes of intermediate-level radioactive liquid waste at ORNL[3] for over five years. One question that arises concerns the capacity of the Conasauga shale, the formation in which the pits are excavated, for adsorbing the liquid waste released to these pits. Investigations were carried out to determine whether it was possible to indicate when breakthrough of large quantities of radionuclides would occur, what would be the breakthrough sequence of radionuclides present in the waste, and, when the pits are abandoned, will the leaching action of rain and ground water remove dangerous quantities of activity from the saturated shale.

The following conclusions developed from this work which used, as a raw material, waste taken from the existing seepage pits.

1. Breakthrough may be predicted by the rise in concentration of Cs^{137}.

2. The order of breakthrough appears to be (1) ruthenium and other unknown radionuclides, (2) trivalent rare earths (TRE), and (3) strontium, soon followed by cesium. However, it should be stated that the TRE and strontium concentrations are very low when compared to the total; therefore sample contamination is difficult to avoid.

3. Leaching by tap water removes very little activity once it is adsorbed on the shale (50 column volumes removed less than 1 per cent).

4. Capacity of the shale for cesium equals 7.7×10^8 dis/min/g.

5. The concentration of ammonia in the effluent from an unsaturated shale column is two to three times higher than the influent concentration before breakthrough. This amount starts to decrease and approach the influent value. Ammonia may be a stable constituent that would serve to indicate the approach of breakthrough of the activity.

6. The shale removes about 15 per cent of the total ruthenium in the waste. Fifty per cent of the remaining ruthenium can be removed by a weak basic type anionic ion-exchange resin.

Conversion of Liquid Wastes to Solids

At HAPO a method is under consideration for the disposal of coating wastes which consists in mixing the aluminum coating wastes with sodium silicate in proper proportions in such a manner that a stiff semisolid gel results, thereby immobilizing the liquid and the contained isotopes.[4] The cost of disposing waste in this form is estimated to be 9 to 13 cents per gallon. This is approximately one-half the cost of the present method of storing it in underground tanks and one-third to one-fourth the estimated cost for new tanks that will be needed about 1960. It also compares favorably with evaporation. The gel would be discharged into a cavern type structure. The excavation would be covered with a concrete roof that would be supported by a concrete footing around the excavation and concrete pillars located in the excavation. Located near the cavern would be the chemical addition system. The coating waste would be pumped from the tank farm and blended with the sodium silicate shortly before being discharged into the cavern. The cavern would also be vented and possibly provided with forced-air circulation. This would enhance the evaporation of water and encourage shrinkage of the gel. Since the evaporation would probably not be accompanied by entrainment, it is not visualized that any radiological hazard would

develop. A filter on the vent would prevent release of radioactive particulates.

The optimum ratio of sodium silicate to aluminate in a waste solution to yield a firm gel[5] is about 2 to 5. A large excess of free caustic is needed in the solution to ensure the formation of a nongranular gel. Suitable gels may be formed from aluminum solutions ranging from 0.3*M* to 0.6*M*. A gel formed from 40 ml of coating wastes stood above a soil column for four months, during which time liquid bled from the gel into the soil. The amount of moisture entering the soil was sufficient to wet 30 in. of the column. Upon sectioning the soil column, it was found that 2.8 per cent of the Sr^{90}, 2.2 per cent of the Co^{60}, and 3.2 per cent of the Cs^{137} in the gel had entered the soil column.

In the last issue of this Review, mention was made of the fluidized-bed calcining of wastes; this work is continuing.[6,7] Pilot plant units are in operation at ANL and ICPP, and a full-scale plant is being designed for Idaho. The Idaho pilot plant has operated successfully for periods up to 357 hr.

Studies of the corrosion of materials which might be used for calciner construction indicate negligible corrosion of Carpenter 20 and type 347 stainless steel for exposure of the order of 400 hr. Carbon steel showed some tuberculation and oxidation when used to transfer heat to the fluid bed. Thermal conductivity of calcined alumina was found to range from 0.08 to 0.23 Btu/hr (ft) (°F) at room temperature and at 1000°F, respectively.

Removal of Specific Fission Products

Iodine

The suppression of iodine emission from gaseous effluents has always been a matter of some concern (see pp. 1–3). A number of studies[8–10] at HAPO are continuing on this problem.

Prior to pinpointing the iodine release as coming from the vessel vent system, the lower bed of a dual-pass silver reactor was given a one-shot regeneration. Later this regeneration proved to have been unnecessary, although the reactor had processed off-gases from more than four times the amount of uranium usually processed by a conventional Purex silver reactor before a breakthrough.

Studies on the exchange rate between iodine in gas phase and solid phase indicate that the rate of exchange of iodine from a gas phase with iodine contained in solid silver iodide appears to be about the same as the rate of reaction of gaseous iodine with metallic silver under comparable conditions of gas temperature, flow rate, iodine concentration, and solid surface. Surfaces having the same geometry and the same quantity of silver deposited over the surface, as silver metal in one case and silver iodide in the other, were exposed to a stream of air (at 300°C, atmospheric pressure) containing 2×10^{-4} atm of I^{131} tracer. The rates of build-up of activity on the two surfaces were nearly equal.

A novel method being studied for the removal of I^{131} from dissolver off-gases involves scrubbing with an organic solvent to remove covalent iodine species from the gas stream. An air-NO_2 mixture containing 0.5 g of iodine was passed through 25 ml of 30 per cent TBP in kerosene without any appearance of iodine in the second trap containing starch indicator. The iodine decontamination factor was estimated to be of the order of 10^4 to 10^5. Most of the iodine was removed from the organic solution by scrubbing with 1.0*M* sodium hydroxide solution.

Cesium

In the last issue of this Review, a number of processes being considered for the removal of cesium from wastes were mentioned. The more promising flow sheets,[10] involving acid-side precipitation of zinc ferricyanide, have

Table IV-2 ACID-SIDE CESIUM RECOVERY* FROM PLANT 1WW

Anion	Zn, M	Cesium recovery, % 1 hr	2 days	4 days	8 days
0.01M ferricyanide	0.02	89	86	80	91
0.01M cobalticyanide	0.02	72	75	80	83
0.005M ferricyanide	0.01	98	97	96	
0.005M cobalticyanide	0.01	94	94	94	

* Conditions: Full-level 1WW used for the first two experiments and 1WW diluted with an equal volume of water for the last two (each neutralized to pH 0).

been tested on a full-level Purex plant with good results. The object of the acid-side approach is to recover cesium without the necessity of first precipitating the iron, aluminum, and uranium. Samples of wastes (5 ml) were neutralized to about pH 0 with sodium hydroxide and then scavenged with either coformed zinc ferricyanide or zinc cobalticyanide, as shown in Table IV-2. Ferricyanide appears to be somewhat better than cobalticyanide in both sets of experiments, and dilute wastes better than full-level.

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The conversion of decontaminated fuel materials into reusable form involves a number of chemical operations. Uranium, thorium, and plutonium from solvent-extraction operations are usually converted from the nitrate solutions into oxides, then to tetrafluorides, and finally to metal. In the case of uranium requiring re-enrichment by gaseous diffusion, the uranium tetrafluoride must be converted to uranium hexafluoride. The enriched or depleted uranium hexafluorides are usually converted back to tetrafluoride and then to metal or oxide for reuse.

uranium tetrafluoride by reaction with hydrogen fluoride gas in fluidized-bed equipment. Both methods employ multiple stages in order to achieve countercurrent gas-solid contact and to permit temperature gradations between inlet and outlet ends. In the stirred fluid-bed reactor under development at the Oak Ridge Gaseous Diffusion Plant, the fluidized powder is mechanically agitated during reaction to prevent channeling of the gas and sintering of the solids.[1] A reinforced spin type agitator is employed. A multistage effect is achieved by connecting

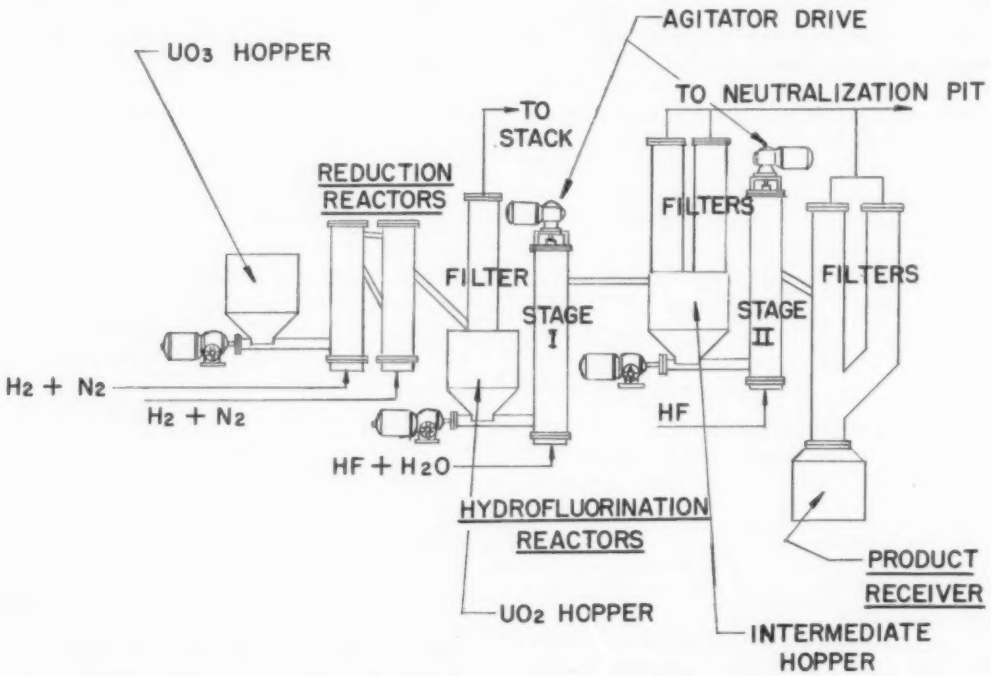

Fig. 2 — Agitated fluidized-bed pilot plant.[1]

Fluidized-bed Production of Uranium Tetrafluoride

Two processes are under development for the continuous conversion of uranium dioxide to

single-stage units in series in a side-by-side arrangement. The complete pilot plant shown in Fig. 2 consists of two reduction stages for production of uranium dioxide and two hydrofluorination stages for conversion of the dioxide to green salt. A hopper and feed screw assembly

was installed between the two hydrofluorination stages to permit removal of the gases and solids from the first stage through a common line. Parallel filters were installed in each of the outlet gas lines to remove entrained solids. The purpose of the agitator is to permit operation of the reactor with pulverized feed materials. Finely powdered solids, such as pot-calcined uranium trioxide and uranium ore concentrates, fluidize poorly without mechanical agitation and are likely to cake during hydrofluorination. The unit has been operated successfully with ground continuous-calciner oxide, pot-calcined oxide, and acid-leached uranium ore concentrate.

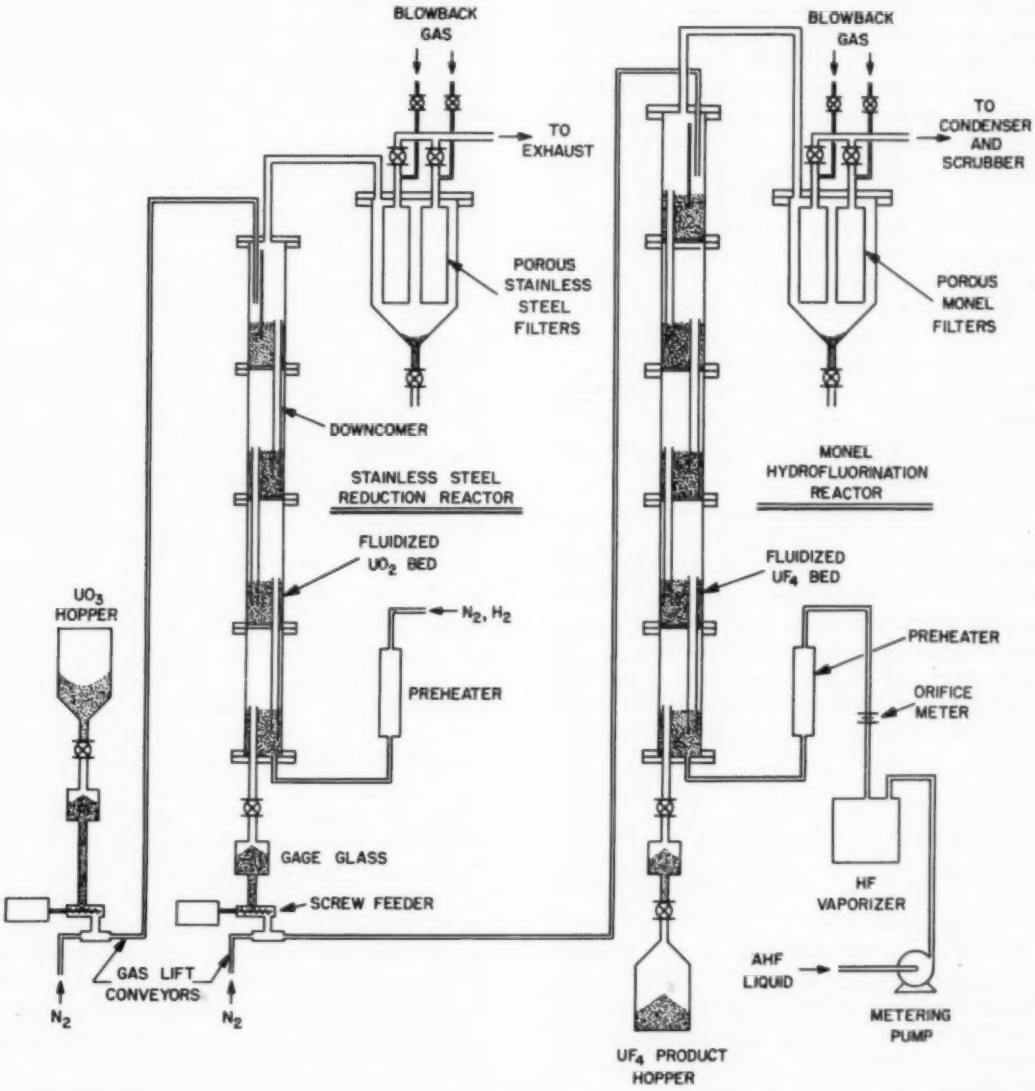

Fig. 3—Schematic diagram of fluidized-bed green salt pilot plant.

A second type of multistage reactor under development employs several fluidized beds[2] in series, one above the other, as shown in Fig. 3.

Each of the beds is supported by a perforated plate, which acts as a gas distributor. The fluidized solids flow by gravity from the upper to the lower stages through downcomer pipes and are discharged by overflow at the bottom. The complete pilot plant, shown in Fig. 3, consists of a four-stage reduction reactor and a five-stage hydrofluorination reactor. By employing a large number of stages, the solids residence time required for a given degree of conversion was reduced. For good fluidization quality in this unit, the feed material should be a granular solid such as the uranium trioxide produced by continuous calcination. Pulverized solids, such as uranium ore concentrates, can be processed after pretreatment to increase the particle size. This has been accomplished by dry briquetting or moist extrusion, followed by crushing and screening. This pilot plant has been successfully operated with fluid-bed calcined uranium trioxide, acid-leached uranium ore concentrate, and carbonate-leached uranium ore concentrate.

Results from both pilot plants indicated that gas-solid contact in the fluid-bed reactors was substantially improved over that obtained in the horizontal screw-agitated reactors currently used in production plants. Satisfactory conversion to green salt has been obtained with very small excesses (5 to 10 per cent) of hydrogen fluoride gas. Uniform and well-controlled temperatures are obtained in the fluidized beds.

Production of Uranium Hexafluoride

A continuous process used in the production of uranium hexafluoride by the reaction of finely divided uranium tetrafluoride with elemental fluorine has been described by Brater and Smiley.[3] Well-dispersed solids and fluorine are introduced into the top of a vertical pipe reactor where the solids and gas react instantaneously. The conversion to uranium hexafluoride is about 99 per cent complete when a fluorine excess of about 20 per cent is maintained. The powder is dispersed in the gas stream with either a vibrating baffle assembly or a rotating spined shaft located at the top of the tower.

Essentially all the reaction occurs in the top 2 ft of the tower, and it is necessary to provide cooling by means of a coil welded to the reactor wall. Water or steam circulated through the coil maintains the tower wall temperature between 850 and 1000°F. The outlet gas stream is cooled and passed through a sintered nickel filter to remove any entrained solids. The uranium hexafluoride is then removed by condensation in a refrigerated cold trap.

Excess fluorine can be recovered in a second reactor, which is designed to operate with an excess of powder so that complete utilization of fluorine can be realized. This unit consists of a vertical tower, a ribbon flight screw cooler, and a sintered nickel outlet gas filter. Since operation at temperatures below 750°F with an excess of uranium tetrafluoride results in the formation of intermediate fluorides that cake on the reactor walls, the temperature of the tower section is maintained between 850 and 1000°F to delay the formation of the intermediate compounds until the temperature is decreased in the cooling screw, where caking is prevented by the scraping action of the flight. The solids discharged from the screw are free flowing and can be conveyed easily to the primary reactor for conversion to hexafluoride.

Recovery of Uranium Hexafluoride from Vent Gases

The vent gases from uranium hexafluoride cold traps necessarily contain a small percentage of uranium hexafluoride owing to the vapor pressure of this material at the cold trap temperature. Experimental studies have shown that a fluidized bed of uranium tetrafluoride can be employed effectively to remove hexafluoride from a gas stream.[4,5] The intermediate compounds (U_4F_{17}, U_2F_9, or UF_5) that are formed can be fed to the fluorination reactors. The best stripping was obtained with a bed temperature of about 400°F, and recovery efficiencies varied from 96 per cent at 100 ppm uranium hexafluoride to better than 99 per cent at 3500 ppm. Very limited data indicated that recovery efficiency did not fall below 99 per cent for gas concentrations as high as 20,000 ppm, although at this concentration actual loss of uranium hexafluoride had increased significantly.

Conversion of Thorium Nitrate to Thorium Oxide

The pilot plant production of thorium oxide of suitable purity for use in nuclear reactor breeding blankets has been carried out using solvent-extracted thorium nitrate solution from the Thorex process.[6] The procedure consists in precipitating thorium oxalate and calcining the oxalate to the oxide. Precipitation was performed by the addition of about 15 per cent excess of reagent grade oxalic acid to a 0.9*M* thorium nitrate solution. The precipitate was filtered on a batch vacuum filter, washed with hot water, and air-dried. Calcination was carried out batchwise in stages at 370, 520, and 800°C to avoid localized overheating due to combustion. The equipment is capable of preparing about 750 lb of thorium oxide per week, and a total of about 11,000 lb has been produced in the pilot plant.

Production of Thorium Metal by Sodium Amalgam Reduction

A continuous process for the production of thorium metal by reduction of thorium tetrachloride with sodium amalgam is under study in equipment designed to produce 2 lb of thorium per hour.[7,8] In this process thorium tetrachloride and sodium amalgam are fed into an agitated vessel where thorium quasi-amalgam is produced continuously. The reaction temperature is about 130°C, and the residence time of the material in the vessel is about 20 min. The product is washed in a continuous wash column with dilute hydrochloric acid to remove by-products and is separated in two amalgamated nickel decanters. The quasi-amalgam is then filtered under pressure through a 3-μ pore size stainless-steel filter to remove excess mercury. The remaining mercury is removed by vacuum distillation and sintering in a large vacuum retort at temperatures up to 1100°C.

Experimental runs have been made in the continuous reduction and washing equipment up to 53 hr in duration in which over 100 lb of thorium was produced. Yields of about 83 per cent were obtained in the reduction step, but losses in the filtration step were high. Laboratory studies are being carried out to find an improved method for removal of the by-products without aqueous washing. Metal produced in the vacuum retort had bulk densities ranging from 7.2 to 9.6 g/cm^3, and the billets contained large central voids. Incomplete removal of chlorides from the quasi-amalgam resulted in high iron and nickel contents in some billets owing to reaction with the retort wall.

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